

A

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THIRD SUPPLEMENT—PART II.

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A DICTIONARY
OF
CHEMISTRY

AND THE
ALLIED BRANCHES OF OTHER SCIENCES.

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THIRD SUPPLEMENT.

PART II.

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PREFACE.

THE second and concluding Part of the EIGHTH VOLUME (or Third Supplement) of this Dictionary brings the Record of Chemical Discovery down to the end of the year 1878, including the more important discoveries which have appeared in 1879 and 1880.

The Author has the pleasure of acknowledging the assistance of the following gentlemen who have contributed Articles to this Part.

H. E. ARMSTRONG, PH.D., F.R.S., <i>Professor of Chemistry at the London Institution</i>	Isomerism.—Naphthalene.—Circular Polarisation (in part).
JAMES T. BROWN, Esq., F.C.S.	Vapour-density.
WALTER FLIGHT, PH.D., <i>of the Mineral Department, British Museum</i>	Meteorites.
G. C. FOSTER, B.A., F.R.S., <i>Professor of Physics at University College</i>	Thermodynamics.
G. F. RODWELL, Esq., F.C.S., <i>of Marlborough College, Wiltshire</i>	Effects of Heat on the Haloïd Compounds of Silver.—Volcanic Products.
ARTHUR SCHUSTER, PH.D., F.R.S., <i>of St. John's College, Cambridge</i>	Spectral Analysis.
T. E. THORPE, PH.D., F.R.S., <i>Professor of Chemistry in the Yorkshire College of Science, Leeds</i>	Specific Volumes.—Water.
R. WARINGTON, Esq., F.C.S.	Nitrification.

DICTIONARY OF CHEMISTRY

THIRD SUPPLEMENT.

(SECOND PART.)

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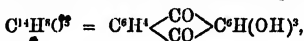
GALACTOSE. See SUGARS.

GALENA. See LEAD SULPHIDE.

GALLIC ACID. *Trioxycarboxylic acid*, $C^6H^6O^5 = C^6H^2(OH)^3CO^2H$, probably 1 : 2 : 4 : 5 (CO^2H in 1), see p. 292.—This acid is formed by the action of melting potash on di-iodosalicylic, di-iodoparaoxybenzoic, bromoprotocatechuic, and monobromodioxycarboxylic acids (Karth a. Senhofer, *Deut. Chem. Ges. Ber.* viii. 754, 1477).

Gallie acid, like salicylic, oxybenzoic, paraoxybenzoic, and protocatechuic acid, is completely oxidised by chromic acid mixture, with rapid evolution of carbon dioxide (Remson, *Sill. Am. J.* [3], v. 354). Dry gallic acid, triturated in a mortar with dry powder of potassium permanganate, takes fire and gives out sparks (Böttger, *Pogg. Ann. Jubelt.* 1874, 156).

A mixture of gallic and benzoic acids, treated with sulphuric acid, yields a compound, $C^{14}H^8O^5$, which is also formed by the action of sulphuric acid on a mixture of pyrogallol and phthalic anhydride. This compound is oxidised by nitric acid, yielding phthalic acid. By oxidation with sulphuric acid and manganese dioxide, it is converted into purpurin, and by reduction with sodium-amalgam into alizarin. Hence it appears to be a tri-hydroxyl-anthraquinone (*anthragallol*),



the three hydroxyls being probably in the relative positions 1 : 2 : 3 (Seuberlich, *Deut. Chem. Ges. Ber.* x. 38).

Gallie acid heated with excess of bromine yields tribromopyrogallol, $C^6Br^3(OH)^3$; by potassium chlorate and hydrochloric acid it is converted into isotríchloroglyceric acid, $C^6H^3Cl^3O^4$; and by the action of potassium permanganate, or its solution in cold water acidulated with sulphuric acid, into a condensation-product, $C^{14}H^{10}O^8$ (pp. 292, 293).

On its reaction with potassium arsenate in contact with the air, see p. 292.

GALLIUM. Ga. Atomic Weight, 69.865 (Lecoq de Boisbaudran, *Compt. rend.* 1875, lxxxi. 493, 1100; 1876, lxxxii. 1036, 1098; lxxxiii. 611, 663, 824, 1044; *Bull. Soc. Chim.* [2], xxv. 521; xxvi. 433; *Ann. Chim. Phys.* [5], x. 100-140; Lecoq de Boisbaudran a. Jungfleisch, *Compt. rend.* lxxxvi. 577; A. Dupré, *ibid.* 720). A metal discovered in August 1875 by De Boisbaudran, in a zinc-blende from the mine of Pierrefitte in the valley of Argolès, Pyrenees; found also in blendes from other localities, especially in the black blende of Bensberg, and the yellow transparent blende from Asturias. To separate it, the mineral, according to its nature, is dissolved in nitrohydrochloric, hydrochloric, or sulphuric acid; plates of zinc are placed in the solution, till the disengagement of hydrogen becomes slow, but is still perceptible, by which means the greater portions of the copper, lead, cadmium, iridium, thallium, silver, mercury, selenium, arsenic, &c., contained in the ore are precipitated; the clear filtered liquid is heated with a large excess of zinc; the resulting gelatinous precipitate, consisting chiefly of alumina, basic salts of zinc, and finally gallium, is redissolved in hydrochloric acid; and the solution is again heated with zinc, whereby a second gelatinous precipitate is obtained, in which the gallium is concentrated in a mass of smaller bulk. This precipitate is redissolved in hydrochloric acid; the solution is treated with hydrogen sulphide; and the filtered liquid, after expulsion of the hydrogen sulphide, is fractionally precipitated with ammonium carbonate, till the solution of the resulting precipitate in hydrochloric acid no longer gives any indication

GALLIUM.

Of the presence of gallium when examined by the spectroscope (*infra*). To complete the separation of the zinc, the precipitated hydroxides and basic salts are dissolved in sulphuric acid, and the solution is cautiously evaporated till the whole or nearly the whole of the free sulphuric acid is expelled; the residue, after cooling, is digested with water till it is dissolved; the nearly neutral solution of the sulphate thus obtained is heated to boiling; the basic gallium sulphate thereby precipitated is filtered off and dissolved in a small quantity of sulphuric acid; the solution is treated with a slight excess of potash, which first precipitates and then redissolves the gallium oxide; and this oxide is precipitated from the alkaline solution by a stream of carbon dioxide. Finally the gallium oxide is redissolved in the smallest possible quantity of sulphuric acid; the solution is mixed with excess of slightly acid ammonium acetate; hydrogen sulphide is passed into the liquid; the filtered acetic solution is diluted with water and heated to boiling, whereby the greater part of the gallium is precipitated as oxide; this precipitate is filtered off, washed with boiling water, and redissolved in sulphuric acid; and the solution is mixed with a slight excess of potash, and filtered, whereby a pure alkaline solution of gallium is obtained.

Metallic gallium is prepared by the electrolysis of this alkaline solution, platinum electrodes being used, and the positive electrode being larger than the negative, on which the gallium is precipitated. A Bunsen's battery of five or six ordinary-sized pairs is sufficient for the electrolysis of 20-30 c.c. of the strong alkaline solution. The precipitated gallium is easily detached by dipping the platinum plate into warm water, and bending it backwards and forwards, or pressing it between the fingers; it may be purified by immersing it for half-an-hour at 60°-70° in dilute nitric acid free from chlorine.

Gallium thus precipitated forms a closely adherent layer, somewhat whiter than platinum, hard, and acquiring a good polish by pressure. When the strength of the current is properly regulated, the metal exhibits a fine, dull, silver-white surface, full of shining points consisting of microscopic crystals. It melts at 30.16°, and therefore at the heat of the hand, and may remain for weeks in a state of surfusion even at temperatures near 0°. In the liquid state it has a fine silvery whiteness, but on touching its surface with a small piece of solid gallium, a spot is formed which rapidly extends, the change being due to the crystallisation of the metal, which in solidifying acquires a decided bluish tinge, with diminished lustre. Distinct crystals may be obtained by dipping into the fused metal, cooled 10°-15° below its melting point, a piece of platinum with a particle of solid gallium attached to it. In from 3 to 10 seconds octahedrons form, modified at the summit by traces of the base OP. If these crystals are not directly removed, the metal becomes heated nearly to its melting point, solidification is retarded, and the basal face is so much developed that large tables are formed. The crystals are brilliant, but difficult to measure on account of their faces being slightly rounded. Gallium is hard, but nevertheless leaves a bluish-grey trace on paper. It has but little malleability, spreads under the hammer, and acquires the polish of the anvil, but soon becomes brittle and splits at the edges. In small bars it exhibits a remarkable degree of solidity, even at a temperature approaching its melting point. In thin sheets, which may be formed by fusing the metal between hot glass plates and detaching it under water after cooling, it can be bent several times at a sharp angle without breaking. Molten gallium readily adheres to glass, forming a mirror whiter than that produced by mercury. It preserves its lustre in the air, even of a laboratory, and in water free from air, but slowly tarnishes in ordinary water.

The specific gravity of gallium is 5.935 at 23° and 5.956 at 24.5° referred to water at the same temperatures.

Gallium heated to bright redness in contact with the air, oxidises merely on the surface, and does not volatilise. It dissolves in *hydrochloric acid* at ordinary temperatures, and more rapidly when heated, with disengagement of hydrogen. It is not sensibly attacked by *nitric acid* in the cold; but with the aid of heat it dissolves slowly, with evolution of nitrous vapours. *Aqueous potash* dissolves it slowly, with evolution of hydrogen.

Spectrum of Gallium.—When induction-sparks $1\frac{1}{2}$ to 2 men. long are passed between a positive external conductor and a negative solution of a gallium salt, a spectrum is produced containing a brilliant violet line (α) at 417 on the scale of wavelengths, and a faint band (β) at 403.1. In a gas-flame gallium shows only the line α , and even this is very faint and fugitive.

Reactions of Gallium Salts.—1. Metallic zinc does not precipitate gallium from acid solutions of its chloride or sulphate, but as soon as the solution has become basic, and the evolution of hydrogen very slow, the gallium is thrown down as an oxide, or more probably a basic salt, in white flocks mixed with basic salts of zinc.

It is therefore in reality a basic salt of zinc which precipitates the gallium; and, to render the latter insoluble, it is sufficient to heat the solution of zinc chloride containing gallium till it gives off hydrochloric acid and becomes basic; the highly concentrated solution may then still appear limpid, but on diluting it largely with water, it deposits zinc oxychloride mixed with gallium. The precipitation of gallium by zinc is slow at ordinary temperatures, not being completed for three weeks or a month when large quantities of solution are operated on, but at the boiling heat it is completed in a few hours. 2. *Cadmium* does not precipitate a solution of zinc chloride rich in gallium, even after long boiling.

3. *Ammonia* in excess forms a precipitate in gallium solutions, but a considerable proportion of the gallium is redissolved; and if the precipitate be dissolved in hydrochloric acid and ammonia again added in excess, the whole of the gallium remains in the ammoniacal solution. Gallium oxide appears to be more soluble in ammonia than alumina, for on repeatedly treating a mixed solution of the chlorides of the two metals with excess of ammonia, the first solutions obtained are rich in gallium, while the last precipitates contain nothing but aluminium. On adding ammonia drop by drop to zinc chloride containing a little gallium, the gallium is precipitated before the zinc, and quickly becomes concentrated in the first deposit, only an inappreciable quantity of it remaining in the mother-liquors.

4. *Ammonium Carbonate* appears to act like free ammonia.

5. *Fixed Caustic Alkalis*.—A small quantity of *potash* precipitates gallium oxide, and then acts like ammonia; but the precipitate is extremely soluble in excess of the alkali.

6. *Alkaline Carbonates*.—Carbonic acid precipitates gallium oxide from its solution in potash. Sodium carbonate precipitates gallium from the solutions of its salts, whether cold or warm. At boiling heat, a very small quantity of sodium carbonate forms in gallium salts a thick precipitate, which redissolves on cooling: this effect is due to the decomposition of neutral gallium salts by hot water, and the recombination of their constituents as the liquid cools. When a solution of zinc chloride containing gallium is fractionally precipitated with sodium carbonate, the greater part of the gallium is found in the earlier precipitates. In a mixed solution of gallium and aluminium also, the gallium is found chiefly in the earlier precipitates, but the separation is less complete than in the case of zinc.

7. *Acetic acid*.—Gallium is not precipitated from the slightly acid solutions of its chloride or sulphate by acid acetate of ammonium, but on heating the liquid, gallium oxide is thrown down in white gelatinous flocks, and does not redissolve, even at the boiling heat, except in presence of a considerable quantity of acetic acid. Nevertheless, if a large quantity of acid ammonium acetate or acetic acid be added, the liquid, when heated, will remain limpid. Neutral sulphate of gallium becomes turbid at ordinary temperatures when treated with a small quantity of acid ammonium acetate; but, on adding a large quantity of that reagent, the liquid becomes clear, and is no longer precipitated on boiling unless diluted with water. An ammoniacal solution of gallium chloride or sulphate is precipitated, whether cold or warm, by an excess of acetic acid, unless the liquid is very dilute, or the quantity of acetic acid added is very large.

8. *Hydrogen Sulphide*.—Slightly acid solutions of gallium chloride or sulphate are not precipitated by hydrogen sulphide, even in presence of acid ammonium acetate; but in slightly acid solutions of zinc chloride containing gallium, a considerable proportion of the latter metal is thrown down, together with the zinc sulphide. The precipitation of the gallium takes place more easily, but is by no means complete, if the solution, rich in zinc, be supersaturated with acid ammonium acetate. If the quantity of zinc in the solution is not sufficient to carry down all the gallium at the first precipitation, more zinc-salt must be added by small portions, till the precipitates, when examined by the spectroscope, no longer exhibit the line Ga α .

In a mixture containing a large quantity of zinc chloride, together with the chlorides of indium and gallium, fractional precipitation with hydrogen sulphide in presence of acid ammonium acetate gives successively: (1) A large quantity of indium, a moderate quantity of zinc, and traces of gallium. (2) A moderate quantity of indium, much zinc, and a notable quantity of gallium. (3) Traces of indium, much zinc, and a notable quantity of gallium.

9. *Ammonium Hydrosulphide* precipitates gallium in presence of zinc salts, both from neutral and from ammoniacal solutions, and does not redissolve it when added in excess, unless the quantity of zinc is so small as to be itself redissolved. When a neutral or slightly acid solution of zinc and gallium is treated with ammonium hydrosulphide containing free ammonia, the gallium is concentrated in the first precipitates of zinc sulphide; but, if the solution of zinc and gallium is ammoniacal,

the gallium becomes concentrated in the later precipitates. Ammonium hydrosulphide does not precipitate the ammoniacal solutions of pure chloride or sulphate of gallium.

also
 effected by fractional precipitation of a quantity of zinc being precipitated together with the gallium.

11. *Potassium Ferrocyanide* gives a yellow precipitate with strongly acid solutions of gallium chloride.

Alloys of Aluminium and Gallium. The alloy obtained when excess of aluminium is heated with gallium to a dull red heat remains quite brilliant, and does not oxidise readily during its preparation. It decomposes water at the ordinary temperature, but more readily at 40° , with formation of a brown powder, which subsequently becomes changed into white flakes of alumina, almost the whole of the gallium being liberated, apparently free from aluminium. The slow evolution of hydrogen from this alloy, is increased by contact with a globule of liquid gallium, an electric couple being formed.

Aluminium and gallium also form liquid and pasty alloys, which oxidise slightly in the air, but decompose water readily. The liquid alloy, when touched with a piece of solid gallium, crystallises in a manner similar to metallic gallium, but it then no longer readily decomposes water (Lecoq de Boisbaudran, *Compt. rend.* lxxxvi. 1204).

Gallium Chloride, GaCl_3 . Chlorine strongly attacks gallium at ordinary temperatures, forming a nearly colourless crystalline chloride, which is very fusible, easily volatile, and absorbs moisture from the air (Lecoq de Boisbaudran a. Jungfleisch). The same compound is formed by dissolving gallium in hydrochloric acid. It is extremely soluble in water, and deliquescent. The residue left on slowly evaporating its solution absorbs moisture from the air, and liquefies, forming a limpid syrup, which remains clear on addition of a very small quantity of cold water, but yields with a larger quantity a copious white precipitate—doubtless an oxychloride—which collects quickly at the bottom of the vessel, redissolves slowly in cold dilute hydrochloric acid, more quickly when the liquid is heated. If a very small quantity of hydrochloric acid be added to dried gallium chloride, the compound dissolves in cold water, forming a solution which becomes turbid when heated and clear again on cooling. A slightly acid solution of the chloride evaporated at a gentle heat deposits needles and crystalline scales which act strongly on polarised light.

Repeated evaporation of solutions of gallium salts with excess of aqua regia is not attended with any loss of gallium by volatilisation of the chloride (De Boisbaudran).

Bromide. The action of bromine on gallium is less energetic than that of chlorine; nevertheless it commences in the cold, with disengagement of heat. The bromide is white and crystalline; less fusible and volatile than the chloride; deliquescent (De Boisbaudran a. Jungfleisch).

Iodide. The combination of iodine with gallium takes place less quickly than that of chlorine or of bromine, and requires the assistance of a gentle heat. The iodide is crystalline, and would doubtless be colourless if quite pure; but it is apt to retain traces of free iodine, and moreover decomposes partially when somewhat strongly heated. It is fusible and volatile, though less so than the bromide; its boiling point is higher than that of iodine, from which it may be separated by distillation in an inert gas. It is deliquescent (De Boisbaudran a. Jungfleisch).

Oxides. Gallium, when heated to bright redness in contact with the air, oxidises, as already observed, merely on the surface. In pure dry oxygen, no perceptible oxidation takes place at 260° ; but at incipient redness, the metal begins to lose its lustre, and becomes covered with a very thin bluish-grey film; at a bright-red heat the coating of oxide becomes more distinct, but it then protects the metal from further action; the oxidation may however be somewhat facilitated by agitation of the liquid metal. A small quantity of the oxide thus formed collects as a sublimate on the cooler parts of the tube.

A more definite product is obtained by ignition of the nitrate (p. 845). The salt, heated to 200° in a current of dry air, decomposes with intumescence, giving off nitrous fumes and leaving a white fritted, very friable mass of oxide. The loss of weight sustained by the nitrate amounts to 63.8 per cent., which is exactly that which should be sustained by a salt having the composition $\text{Ga}(\text{NO}_3)_3$ or $\text{Ga}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5$, when completely resolved into nitric anhydride and sesquioxide, supposing the atomic weight of gallium to be 69.865.

The sesquioxide heated to cherry-redness in a current of pure dry hydrogen, partly sublimes undecomposed, and is partly reduced to a bluish-grey fritted substance exactly

like that which is formed by the direct oxidation of gallium. This lower oxide dissolves in nitric acid without evolution of nitrous fumes, and in dilute sulphuric acid without evolution of hydrogen; it is therefore free from metallic gallium, and probably consists of the monoxide. It reduces potassium permanganate. At a bright red heat the oxide is partly reduced to the metallic state.

Nitrate, $\text{Ga}(\text{NO}_3)_3$. The strongest nitric acid (sp. gr. 1.52) free from nitrous vapours scarcely attacks gallium at ordinary temperatures, but at 40° – 50° the action takes place and goes on regularly, with formation of a grey deposit which takes a long time to dissolve. On evaporating the solution to dryness, and heating the residue to 110° , it partly decomposes; and on dissolving the unaltered portion in water, and evaporating the filtered solution over the water-bath, the nitrate is obtained as a white, compact, very deliquescent mass, which exhales the odour of nitric acid. By evaporation in a dry vacuum or in a stream of dry air at 40° , the water and excess of nitric acid are expelled, and the pure nitrate is obtained. At higher temperatures it is completely decomposed, leaving a residue of sesquioxide (Dupré).

Sulphates. The *sesquisulphate* or *Gallie sulphate*, $\text{Ga}_2(\text{SO}_4)_3$ [mode of preparation not described], is non-deliquescent, but very soluble in water. The concentrated solution is syrupy. A perfectly neutral solution is decomposed by boiling, very little gallium remaining dissolved, provided the solution is sufficiently diluted. On cooling, the precipitate dissolves completely. By slow evaporation, or by the cooling of a strong solution, the sulphate is obtained in soft nacreous scales, sometimes grouped in stellate or radiate masses. It dissolves in alcohol of 60 per cent., but is insoluble in ether. On evaporating an acid solution of the sulphate, and drying the residue till it ceases wholly or nearly to give off white vapours of sulphuric acid, the salt does not lose its solubility in water or in weak alcohol, but it takes some time to dissolve (De Boisbaudran).

The salt obtained by dissolving the lower oxide of gallium in dilute sulphuric acid reduces potassium permanganate (Dupré).

Gallium-ammonium Alum is obtained by slow evaporation of an acid solution of gallie sulphate neutralised with ammonia, or by mixing the solutions of gallie sulphate and ammonium sulphate, and evaporating. It crystallises in cubes with octohedral facets, or in octohedrons with cubic facets, having exactly the appearance of ordinary alum, and capable, like the latter, of forming supersaturated solutions which solidify instantly when touched with a small crystal of the salt. A strong solution of the alum becomes slightly turbid when boiled, but clear again on cooling. Very dilute solutions when boiled yield a copious precipitate, probably a basic salt, and if the liquid be filtered while hot, only a trace of gallium remains dissolved. The precipitation on boiling is prevented by the addition of a drop of sulphuric acid, or of a certain quantity of acetic acid (Lecoq de Boisbaudran).

Atomic Weight and Quantivalence of Gallium. The existence of the alum just described shows that gallium is analogous to aluminium, forming a sesquioxide Ga_2O_3 , a trichloride GaCl_3 , &c. &c. This being established, the atomic weight of the metal may be determined by the analysis of the alum or of the nitrate. Now (a) 3.1044 grams of the alum gave on ignition 0.5885 of sesquioxide, whence may be deduced for gallium the atomic weight 70.032. (b) 0.4481 grams of the metal yielded, by conversion into nitrate and ignition of that salt, 0.6024 grams of oxide, which gives for gallium the number 69.698. The mean of these results, 69.865, may be taken as a near approximation to the true value (Lecoq de Boisbaudran, *Compt. rend.* lxxxvii. 941).

The specific heat of gallium between 12° and 23° , as determined by Berthelot (*Compt. rend.* lxxvi. 786), is 0.079, which, multiplied by the atomic weight, gives the product 5.52, a number not differing greatly from the mean value (6.4) of the atomic heats of the metals. The specific heat of liquid gallium, between 106° and 119° , is 5.59, differing therefore but slightly from that of the solid metal; in this respect gallium resembles mercury, bismuth, and some other metals.

Mendelejeff (*Compt. rend.* lxxxi. 969) points out that, according to the periodic relation which has been shown to exist between the chemical functions of the elements and their atomic weights (2nd *Suppl.* 462), there should exist an element intermediate between aluminium (27) and indium (113). This element, which he designates as *ekaluminium*, should have the atomic weight 68, and specific gravity 5.9; should be easily reducible, precipitated by hydrogen sulphide more readily than zinc, precipitated also by barium carbonate, and recognisable by the spectroscope. These properties are regarded by Mendelejeff as sufficiently near to those of gallium to justify the conclusion that the latter is really the suspected *ekaluminium*.

De Boisbaudran, on the other hand, while admitting the great importance of the relations suggested by Mendelejeff, points out that the properties of gallium are not

in all respects intermediate between those of aluminium and of indium: thus the sesquioxide of gallium is more soluble in ammonia than either indium oxide or alumina, which in fact are nearly insoluble in that reagent. Moreover gallium oxide is precipitated by sodium carbonate before alumina and likewise before indium oxide. The extreme fusibility of gallium (also is difficult to reconcile with the degree of fusibility which it should exhibit according to the theory in question (*Ann. Chim. Phys.* [5] x. 138).

GARDENIN. A neutral substance obtained by Stenhouse in 1856 (*Phil. Trans.* cxlvi. 155) from dekamali gum, a resinous exudation from *Gardenia lucida* (p. 627), and further examined by Stenhouse & Groves (*Chem. Soc. J.* 1877, i. 551). It is extracted from the resin by boiling with alcohol, and separates on cooling in long, light-yellow needles, which must be washed with cold spirit to purify them from an amorphous greenish-yellow resin which forms the greater portion of the dekamali gum, then repeatedly crystallised from alcohol, agitated several times with light petroleum to remove a colourless fatty substance, and finally purified by alternate crystallisation from hot benzene and from alcohol.

Gardenin thus purified forms brilliant deep-yellow crystals, melting at 163° – 164° . When dried at 100° , it gave by analysis 61.91 per cent. carbon and 5.45 hydrogen (mean), agreeing nearly with the empirical formula $C^6H^5O^2$.* It is decomposed by boiling with nitric acid, but does not yield picric acid. Its solution in 30 parts of boiling glacial acetic acid, treated, after cooling, with nitric acid of specific gravity 1.45, yields gardenic acid, a non-azotised crystalline substance, which melts at 236° , is insoluble in water and in dilute acids, but dissolves readily in alkalis, and is reprecipitated therefrom by acids. It is very slightly soluble in boiling spirit, more soluble in glacial acetic acid, from which it separates in the crystalline state.

GARNET. A. v. Lasaulx (*Jahrb. f. Min.* 1875, *149) describes crystals of garnet from Geyer in Saxony, exhibiting, together with ∞O_2 , the form ∞O_3 , hitherto observed only in garnets from Auerbach on the Bergstrasse. According to A. Wichmann (*Pogg. Ann.* lvi. 282; *Jahrb. f. Min.* 1876, 198; *Chem. Soc. J.* 1876, ii. 51, 178), the dark-coloured massive garnet, called *allechroïte*, is partly amorphous and partly possesses double-refracting structure, as formerly observed by Des Cloizeaux in grossularia.

The following are recent analyses of garnets: (1–3) occurring in the eclogites of Upper Franconia (p. 703). 1. Large distinct garnets from Eppenreuth near Hof. 2. Large garnets, seldom crystallised, from Silberbach, near Conradsreuth. 3. Garnet in very numerous grains from Falser Höhe near Markt Schorgast (E. v. Gerichten, *Liebig's Annalen*, clxxi. 183). (4–6). Red garnet from the serpentine of Zöhlitz, Großendorf, and Waldheim in Saxony (Lemberg, *Zeitschr. geol. Ges.* xxvii. 531). 7. Spessartin, from S. Marcel, in Piedmont, where it occurs, together with marcelin, piemontite, red mica, and quartz, in light-yellow, seldom orange-yellow crystals, ∞O_2 , the nucleus of which often consists of marcelin; sp. gr. = 4.01 (Pisani, *Compt. rend.* lxxxiii. 167).

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO	H ² O	
1.	43.37	23.13	—	14.63	0.98	13.48	4.78	—	= 100.37
2.	43.16	23.04	—	14.60	0.91	13.64	6.05	—	= 101.30
3.	41.45	16.15	11.50	12.40	0.91	10.51	8.36	—	= 101.28
4.	39.62	22.96	10.96	—	—	4.40	21.24	0.82	= 100
5.	40.60	22.70	9.34	—	—	4.23	21.47	1.66	= 100
6.	40.44	23.11	9.96	—	—	4.82	20.70	1.47	= 100
7.	38.50	18.40	2.70	—	34.25	5.87	—	—	= 99.72

On the garnet-olivine rock of the Saxon Granulite District, see Dathe (*Jahrb. f. Min.* 1876, 325; *Chem. Soc. J.* 1876, ii. 387).

GASES. *Absorption by Metals.*—The solution of gases in iron, steel, and manganese has been investigated by Troost & Hautefeuille (*Ann. Chim. Phys.* [5], vii. 155) with the following results:

1. Cast-iron kept in fusion in contact with silica or silicates, evolves carbon oxide resulting from the action of iron carbide on silica, the iron, consequently, becoming poorer in carbon and richer in silicon.

2. Melted cast-iron dissolves considerable quantities of hydrogen, the solubility of the gas being diminished by the presence of silicon, and much increased by the presence of manganese.

3. Carbon oxide is much less soluble than hydrogen in the different varieties of

* Füllciger, who also analysed gardenin (*Pharm. J. Trans.* [3], vii. 589), assigned to it the formula $C^{12}H^{10}O^{12}$, but as his product was purified merely by repeated crystallisation from spirit, it was probably still contaminated with the fatty substance above mentioned.

cast-iron. Its solubility is diminished or even annulled by the presence of manganese.

4. Pig-iron, after cooling, retains gases which may be extracted by heating the metal to a temperature not exceeding 800° . Hydrogen is always more abundant than carbon oxide, both in the solid and the fused metal, and is more persistently retained by the metal. Manganiferous iron retains more hydrogen than does ordinary cast-iron.

5. Steel dissolves less gas than cast-iron, hydrogen predominating over carbon oxide, and being more forcibly retained by the metal.

6. Soft iron, on the contrary, dissolves more carbon oxide than hydrogen, and retains it more forcibly.

7. Finely-divided pure iron, deprived of gases, decomposes water slowly at the ordinary temperature, and rapidly at 100° , the decomposition being more rapid the finer the state of division of the iron.

The solubility of carbon oxide in cast-iron, malleable iron, or steel, may be estimated by the action of moist mercuric chloride in a vacuum at ordinary temperatures. By this mode of proceeding it is possible to determine the limit of temperature above which the gases taken up by the iron are partly due to chemical reactions.

Absorption by Saline Solutions.—The absorptive powers of solutions of the chlorides of ammonium, potassium, sodium, barium, strontium, and calcium for carbon dioxide have been determined by J. J. Mackenzie (*Ann. Phys. Chem.* [2], i. 438) with the following general results:

(1). Saline solutions absorb less carbon dioxide than an equal volume of water. (2) The volume of gas absorbed decreases as the concentration of the solution increases. (3). Different solutions possess different absorption-coefficients. The absorption-coefficient for potassium chloride, like its molecular weight, lies between those for sodium and ammonium chlorides, and that of strontium between those for barium and calcium chlorides. (4). The coefficient varies with the temperature almost in the same manner as for pure water.

The absorption of carbon dioxide by sulphuric acid and its mixtures with water, at 17° , has been investigated by J. Satschenow (*Petersb. Acad. Bull.* xxii. 102). The absorption-coefficient of undiluted H^2SO^4 (0.932) is so near to that of water (0.9519 at 17° , according to Bunsen), that there can be no doubt of the actual identity of the two. By dilution the absorption-coefficients are diminished, very rapidly at first, the minimum value 0.666 being attained at $\text{H}^2\text{SO}^4 + \text{H}^2\text{O}$, beyond which the coefficients increase slowly on further dilution.

Diffusion of Gases.—J. Clerk Maxwell (*Phil. Mag.* [4], xlv. 453) has studied the phenomena of gaseous diffusion in connection with molecular movement. According to the mechanical theory of gases (iii. 131), this movement of the gaseous molecules goes on in air apparently at rest, as well as in gases which are diffusing one into the other. This movement of the molecules in a stratum of air cannot of course be observed directly, but its existence may be inferred from the following considerations. When a horizontal stratum of air moves onward, the molecules which diffuse out of it into the strata immediately above and below it, endeavour to impart their horizontal velocity to the molecules of these other strata, while the molecules which diffuse from the latter into the moving stratum tend to retard its motion and bring it to rest. This mutual action of contiguous gas-strata is similar to the friction of two rough surfaces, one of which slides over the other, and to the internal friction of liquids called *viscosity*. It is, in fact, only another kind of diffusion, namely, a lateral diffusion of momentum, and the relative values of the friction of different gases may be deduced from observations on the so-called transpiration of gases through narrow tubes, while the absolute values are deduced from Meyer's observations on the oscillation of horizontal discs in gases (*Pogg. Ann.* cxliii. 14; *Jahresb. f. Chem.* 1871, 44).

Another method of demonstrating the diffusion of molecules in still air is to warm the upper layer and observe the proportion in which the heat thus imparted is communicated to the lower layers. This is, in fact, a third kind of diffusion—the diffusion of energy.

All three kinds of diffusion, viz. diffusion of matter, diffusion of momentum (friction), and diffusion of energy (heat-conduction), are brought about by the movement of the molecules. The greater the velocity of the molecules, and the farther they travel before their course is arrested by collision with other molecules, the more rapid will be the diffusion. As the velocity of the molecules is known, it is possible to calculate, from Loschmidt's experiments on diffusion (*2nd Suppl.* 542), the average distance traversed by a molecule before it strikes against another, or the mean path between two collisions, and thence also the number of collisions which each molecule experiences in a second of time.

Molecular Relations.

	Hydrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
Mass of molecule	1	16	14	22
Mean velocity at 0° per second in meters	1859	465	497	396
Mean path in $\frac{1}{10,000,000}$ mm.	965	560	482	379
Number of collisions in millions per second	17750	7646	9489	9720
Diameter of molecule in $\frac{1}{10,000,000}$ mm.	5.8	7.6	8.3	9.3
Mass in $\frac{1}{25,000,000}$ mgrms.	40	736	644	1012

Diffusion Relations.—Measure = $\frac{(\text{Centimeters})^2}{\text{Seconds}}$

	Calculated	Observed	
Hydrogen and Oxygen	0.7086	0.7214	Diffusion of matter observed by Loschmidt (2nd Suppl. 542).
Hydrogen and Carbon Monoxide	0.6519	0.6422	
Hydrogen and Carbon Dioxide	0.5575	0.5558	
Oxygen and Carbon Monoxide	0.1807	0.1802	
Oxygen and Carbon Dioxide	0.1427	0.1409	
Carbon Monoxide and Dioxide	0.1386	0.1406	Diffusion of momentum.*
Hydrogen	1.2990	1.49	
Oxygen	0.1884	0.213	
Carbon Monoxide	0.1748	0.212	
Carbon Dioxide	0.1087	0.117	
Air		0.256	Diffusion of temperature.†
Copper		0.077	
Iron		0.183	
Cane-sugar in water		0.00000365	
(or in 1 day)		0.3144	
Salt in water		0.00000116 §	

Change of Temperature attending the Diffusion of Gases through Porous Partitions.—

The following observations have been made by Dufour (*N. Arch. ph. nat.* xlv. 9; xlix. 101-33). (1). When a dry stream of air, hydrogen, or coal-gas penetrates the walls of a porous vessel, or passes through a vessel containing fragments of the porous material, a fall of temperature takes place, which gradually becomes smaller and smaller, and at length disappears. (2). When moist streams of these gases circulate under the same conditions, a rise of temperature is produced, which likewise diminishes and finally ceases. (3). The heating is probably due to the absorption of aqueous vapour by the porous substance; the cooling to the evolution of that vapour, these effects being greater or less according to the previous state of the porous vessel. (4). When air on the one side and hydrogen or coal-gas on the other are in contact with a porous partition, and diffusion takes place without alteration of pressure, a rise of temperature is produced on that side of the partition towards which the stream of gas is directed, that is to say on the side in contact with the lighter gas, and a fall of temperature on the other. (5). These changes of temperature appear to occur, not in the entire mass of the gas, but only at the surface of the porous partition, the heating on the one side being due to the condensation of the gas, and the cooling on the other to its expansion. (6). When the diffusion is accompanied by variation of pressure, the effects are complicated by the alterations of temperature directly resulting from increase or diminution of pressure (Dufour).

Thermo-diffusion.—C. Neumann infers, from theoretical considerations, that when a finite portion of a gas enclosed in a tube of infinite length (or returning into itself) has a density greater or less than that of the rest of the gas, a difference of temperature artificially produced at the two extremities of this finite portion must give rise to a continuous movement in the whole of the endless cylinder of gas, directed from the cold to the warm end through the finite portion above mentioned, supposing that the gas in this portion is of greater density than the remainder (*Jahresb. f. Chem.* 1874, 15).

* Graham (*Phil. Trans.* 1849, ii. 349; *Phil. Mag.* [3], xxxv. 541; [4], xxvi. 409); O. E. Meyer, *Pogg. Ann.* cxxv. and cxxvii.; *Jahresb. f. Chem.* 1871, 44).

† Stefan, *Wien. Akad. Ber.* [2 Abth.], lxx. 45-59.

‡ Voit, *Pogg. Ann.* cxxx. 227, 293; *Jahresb.* 1867, 95.

§ Fick, *Pogg. Ann.* cxxxv. 337.

Experiments made by W. Fenderson (*Phil. Mag.* [4], xlv. 55), in accordance with the requirements of this theory, on a portion of the gas enclosed between diaphragms of platinum or palladium sponge, gypsum, or *magnesia usta*, have shown that it appears to be a universal property of porous bodies, when used as diaphragms, to draw gas through themselves from the colder to the warmer sides. This *thermo-diffusion* differs from ordinary diffusion, inasmuch as it takes place between two portions of the same gas on opposite sides of a diaphragm. It is the correlative of the phenomenon observed by Dufour, in whose experiments a change of temperature results from diffusion, whereas in those of Fenderson, diffusion is produced by change of temperature, and in such a direction that the artificially excited change of temperature is diminished by that which, according to Dufour's law, results from the diffusion itself.

• *Hygrometric Diffusion.*—(1). When a porous partition (the porous cell of a voltaic battery) separates two portions of air of different degrees of moisture, two opposite and unequal streams of air pass through it, the stronger current being directed from the dry to the moist air, and the difference in strength of the two depending chiefly on the difference of vapour-tension on the two sides of the partition. Temperature has little or no direct influence on the result. (2). Hygrometric diffusion takes place also, though less quickly, through dense and very homogeneous plates of marble (5 mm. thick), polished or unpolished; also through plates of gypsum, alabaster, and retort-charcoal. On account of the greater porosity of gypsum, diffusion through it can give rise only to slight differences of pressure on the two surfaces, and even these differences are quickly equalised. Alabaster is much less penetrable by gases than gypsum or marble, and diffusion through it takes place much more slowly. (3). When a limited volume of air is confined in a vessel, part only of which is porous, a difference of hygrometric state between the inner and outer air leads to a difference of pressure, which is independent in amount on the extent of the porous part of the side of the vessel, but is longer in establishing itself as the proportion of porous to compact surface is smaller. (4). The difference of pressure produced by hygrometric diffusion depends, under otherwise similar circumstances, on the thickness of the partition, and in the case of porous clay is nearly in the inverse ratio of the square root of the thickness (limits of observation 3 to 10 mm.) (5). The excess of the diffusion-current of dry air attains its greatest value when the pressure on the two sides of the partition remains equal. This excess, which varies with the nature of the porous partition and the hygrometric conditions of the experiment, is greater in proportion as the thickness of the partition is less. With thicknesses of 3.1 mm., 5.1 mm., and 9.1 mm., it was found to vary as 100 : 72 : 51. (6). When hygrometric diffusion gives rise to a difference of pressure on the two sides of the partition the excess of volume of the stronger current diminishes as the difference of pressure increases. This decrease is quicker as the thickness of the partition is greater (Dufour, *N. Arch. ph. nat.* xlv. 9; liii. 177-210).

Passage of Gases through Liquid Films and Colloid Membranes.—F. Exner (*Pogg. Ann.* clv. 321, 443; *Chem. Soc. J.* 1876, ii. 163) has studied this mode of diffusion by introducing into a diffusion-tube a film of soap formed with a solution of 1 part by weight of dried Marseilles soap in 60-80 parts of distilled water. Experiments were made with air and coal-gas, air and carbon dioxide, air and hydrogen sulphide, air and ammonia, air and oxygen, air and nitrogen, coal-gas and oxygen, coal-gas and hydrogen, nitrogen and hydrogen. A comparison of the velocities with which the gases traversed the film led to the conclusion that the passage of the gases through the film is due, partly to their absorption by the liquid and subsequent elimination from it, partly to simple diffusion through the film, as through a porous partition of extremely small thickness. On this supposition the diffusion-velocity, α , of a gas

must be represented by the expression $\frac{C}{\sqrt{\delta}}$, where C is the absorption-coefficient of the gas for water and δ its density. The following table shows the agreement of the values of α calculated from this formula with those deduced from actual observation:—

Gas	Coefficient of absorption	Density	$\frac{C}{\sqrt{d}}$	α observed	α calculated
Nitrogen	0·015	0·97	0·0153	0·86	0·85
Air	0·017	1·00	0·017	—	1·00
Oxygen	0·030	1·106	0·0285	1·95	1·60
Coal-gas	0·025	0·480	0·036	2·27	2·12
Hydrogen	0·019	0·070	0·072	3·77	3·89
Carbon Dioxide	1·002	1·52	0·812	47·1	45·1
Hydrogen Sulphide	3·165	1·17	2·94	165	163·3
Ammonia	700	0·59	903·0	46000	54450

According to Barthélemy (*Compt. rend.* lxxvii. 427), the natural colloïdal surfaces of plants exert upon mixed gases a dialytic or separating action similar to that observed in caoutchouc by Graham (1st Suppl. 632), transmitting carbon dioxide thirteen times as readily as nitrogen, and six or seven times as readily as oxygen.

Diffusion of Gases through Absorbing Substances (Wroblewski, *Ann. Phys. Chem.* clviii. 539-568, and [2], i. 438-451).—When an absorbable gas is suddenly brought in contact with the surface of a liquid contained in a cylindrical or prismatic open vessel, and not disturbed by currents arising from variations of temperature, the uppermost layer of the liquid will of course be first saturated by the gas; and Wroblewski's experiments show that the diffusion of the gas through the liquid takes place according to Biot's Law of Difference, the gas passing successively from each layer of liquid to the one next below it, and the rate at which this movement takes place being proportional to the difference of saturation of the two layers. When carbon dioxide is brought in contact with an aqueous solution containing in 100 c.c. more than 10 grams of dry sodium chloride, or 26·98 sugar, the gas diffuses itself through the liquid exactly according to the Biot-Fourrier law of heat-conduction, the quantities of gas absorbed being proportional to the square roots of the times of absorption, and the liquid acting, with regard to the diffusion of the carbon dioxide, just like a solid body with regard to the conduction of heat. With weaker solutions and with pure water, the regularity of the diffusion is disturbed by the increase of density of the liquid charged with carbonic acid, which consequently sinks to the bottom, thereby completely altering the conditions of the diffusion. The Biot-Fourrier law of diffusion likewise holds good in glycerin and its aqueous solutions; also in strong solutions of colloïd substances, such as gelatin, even when they contain a quantity of the colloïd sufficient to render them viscous or semi-solid; a perfectly dry hard plate of gelatin, on the other hand, is impervious to carbon dioxide.

Former experiments by Wroblewski (*Pogg. Ann.* lviii. 539-568) showed that the rate at which carbon dioxide or hydrogen diffuses through a caoutchouc membrane is proportional to the pressure of the gas upon the membrane: this is merely a particular case of the law above stated.

From these results Wroblewski deduces the following law: *When a gas is absorbed by any substance, liquid, solid, or semi-solid, it diffuses itself in the absorbing body according to laws identical with those which regulate the propagation of heat in a solid rod.* The only exceptions to this law are those which are due to the action of gravity.

Aspiration and Migration of Gases.—These terms are applied by F. Bellamy (*Compt. rend.* lxxxiii. 669) to denote the passage of gases enclosed over mercury through the capillary tubes of cotton or linen skeins, hemp, hay, rushes, strips of caoutchouc and many other bodies. When separate portions of the same gas under different pressures are connected by such bodies, the level of the mercury comes to rest only when the pressure on the two sides is equalised. When different gases, such as hydrogen and carbon dioxide, are connected by a skein of cotton-thread, &c., enclosed in a bent glass tube, streams of the two gases pass through the skein in opposite directions till the pressure of each gas on the two sides becomes equal, the hydrogen travelling the faster of the two.

Friction of Gases. O. E. Meyer in 1865 and 1866 (*Pogg. Ann.* cxv. and cxvii.) showed, by experiments on circular discs vibrating horizontally round a vertical axis, and by calculation from Graham's experiments on the transpiration of gases through capillary tubes (ii. 820), that the constant of the internal friction of air is independent of pressure, and increases with the temperature. This result was confirmed in a similar manner by Maxwell (*Phil. Trans.* 1866), who had previously deduced it from theoretical considerations (*Phil. Mag.* [4], xix. 31).

Meyer found, from his first experiments, as an approximate result, that the value of the friction-coefficient of air μ_t between 0.00018 and 0.00027. Subsequently (*Pogg. Ann.* cxliii. 14), by experiments made at various temperatures, he inferred that the temperature-coefficient for the friction is about $\frac{1}{2}$ the coefficient of expansion, so that, representing the coefficient of expansion at the temperature t° by μ_t , and the temperature-coefficient of friction by β , we have,

$$\mu_t = \mu_0(1 + \beta t)$$

where $\beta = \frac{1}{2} \times 0.003665 = 0.002749$.

By a series of experiments made at different temperatures, the value of μ_0 was found to be between 0.000168 and 0.000174.

A. v. Obermayer (*Wien. Acad. Ber.* [2to Abth.], lxxi. 281–308), from a comparison of his own experiments on vibrating discs with those of Meyer and Maxwell, deduces the values $\beta = 0.002723$; $\mu = 0.00016747$, according to which the expression for the friction-coefficient of air becomes:

$$\mu_t = 0.00016747(1 + 0.002723 t).$$

The same methods of investigation have been applied to the determination of the friction-coefficients of a considerable number of gases by Meyer (*Pogg. Ann.* cxliii. 14; *Jahresb. f. Chem.* 1871, 44); by Meyer a. Springmühl (*Pogg. Ann.* cxlviii. 526–549; *Jahresb.* 1873, 16); and by A. v. Obermayer (*Wien. Acad. Ber.* [2to Abth.], lxxiii. 433–474; *Jahresb.* 1876, 42). The results are given in the following table, together with those calculated by Meyer from Graham's transpiration experiments:

Friction-coefficients of Gases.

	Meyer a. Springmühl		Obermayer		Friction-coefficient referred to that of Oxygen = 0.0001873 calculated from Graham's Transpiration experiments
	Transpiration-coefficient	Friction-coefficient at 0°	Transpiration-coefficient	Friction-coefficient at 0°	
Oxygen	1.000	0.000212	1.000	0.0001873	0.0001873
Air	0.899	190	0.896	1678	1683
Nitrogen Dioxide	0.878	186	—	—	1645
Nitrogen	0.873	184	0.885	1659	1635
Carbon Monoxide	0.870	184	0.868	1625	1630
Carbon Dioxide	0.755	160	0.738	1383	1414
Nitrogen Monoxide	0.752	160	0.723	1353	1408
Hydrogen Chloride	0.736	156	—	—	1379
Chlorine	0.687	147	—	—	1287
Sulphur Dioxide	0.654	138	—	—	1225
Hydrogen Sulphide	0.616	130	—	—	1154
Marsh-gas	0.555	120	—	—	1040
Methyl Chloride	0.547	116	—	—	1025
Ethylene	0.516	109	0.492	922	966
Ammonia	0.511	108	—	—	957
Cyanogen	0.506	107	—	—	948
Ethyl Chloride	0.499	105	0.475	889	935
Methyl Oxide	0.483	102	—	—	905
Hydrogen	0.439	093	0.459	861	822

The following is a comparison of the transpiration-coefficients of air, oxygen, hydrogen and carbon dioxide, as determined by different observers:

	Air	O ²	H ²	CO ²
Graham *	1	1.113	0.488	0.840
Maxwell †	1	—	0.516	0.859
O. E. Meyer ‡	1	1.095	0.601	0.851
Lang §	1	—	—	0.830
Obermayer	1	1.116	0.513	0.824
Kundt a. Warburg	1	—	0.488	0.804

* This Dictionary, vol. ii. p. 820.

† *Wien. Acad. Ber.* [2 Abth.], lxxii. 604.

‡ p. 847 of this volume.

§ *Pogg. Ann.* cxlviii. 1.

|| *Deut. Chem. Ges. Ber.* 1876, 160.

With respect to the alteration of their friction-coefficients according to temperature, gases may be arranged nearly in the same order as with reference to their coefficients of expansion:

	Friction-coefficient according to Obermayer	Expansion-coefficient according to Regnault
Air	$\eta = 0.0001678(1 + 0.003665t)^{0.76}$	0.003671
Hydrogen	$0.861(1 + 0.003665t)^{0.79}$	0.003661
Oxygen	$1.878(1 + 0.003665t)^{0.80}$	—
Carbon Monoxide	$1.625(1 + 0.003665t)^{0.74}$	0.003669
Ethylene	$0.922(1 + 0.003665t)^{0.96}$	—
Nitrogen	$1.559(1 + 0.003665t)^{0.74}$	—
Nitrogen Monoxide	$1.353(1 + 0.003719t)^{0.93}$	0.003719
Carbon Dioxide	$1.383(1 + 0.003701t)^{0.94}$	0.003710
Ethyl Chloride	$0.889(1 + 0.003909t)^{0.98}$	—

From these results it appears that the friction-coefficient of the less easily condensable gases (till lately regarded as uncondensable) is nearly proportioned to the $\frac{2}{3}$ power, and that of the more easily condensable gases to the first power, of the absolute temperature. For temperatures between 150° and 300° , air gave the same values of the exponent as between the lower temperatures— 21.5° and 53.5° . Carbon dioxide exhibited a slow decrease of the exponent with the temperature.

Nearly equal values of the exponent for air, carbon dioxide, and hydrogen have been obtained by J. Puluj (*Wien. Acad. Ber.* [2 Abth.], lxxiii. 589), viz. for air 0.722; for carbon dioxide 0.917, and for hydrogen 0.693.

From the friction-coefficients may be deduced the following lengths of the *medium paths* (p. 847) of a molecule:

	Obermayer	Stefan, Loschmidt	Maxwell, Graham
Air	0.0000074 cm.	71	83
Hydrogen	144	139	153
Oxygen	79	74	87
Carbon Monoxide	73	65	81
Carbon Dioxide	49	50	56
Nitrogen Monoxide	48	42	56

On the Friction of Rarefied Gases, see Kundt & Warburg (*Pogg. Ann.* clv. 337-365 and 525-550; *Phil. Mag.* [4], l. 53; *Jahresh. f. Chem.* 1875, 33); A. Kundt (*Pogg. Ann.* clviii. 568-572 and 660; *Jahresh.* 1866, 41).

On the Friction of Air on Glass, see Warburg (*Pogg. Ann.* clix. 399-415; *Jahresh.* 1876, 41).

E. Wiedemann (*N. Arch. ph. nat.* lvi. 277) has also determined the friction-coefficient of gases at different temperatures, by the velocity of their flow through capillary tubes. The following table gives the results referred to air at $8^{\circ} = 100$.

	8°	100°	184.5°
Air	100	123.1	141.1
Carbon Monoxide	56.87	—	136.1
Carbon Dioxide	80.48	104.8	123.4
Nitrogen Monoxide	80.41	105.6	124.1
Ethylene	56.24	73.89	87.38

For air and carbon monoxide on the one hand, and for carbon dioxide and nitrogen monoxide on the other, which latter have equal molecular weights, the friction increases with rise of temperature in the same ratio. The friction-coefficient μ_t at the temperature t , being equal to $\mu_0 (1 + 0.003665t)^n$, the exponent n is found to have the following values, which are not the same for all gases, and do not all vary with the temperature according to the law laid down by Obermayer:

	0° to 100°	0° to 184.5°	100° to 184.5°
Air	0.7333	—	0.6701
Carbon Monoxide	—	0.6949	—
Carbon Dioxide	0.9296	—	0.8024
Nitrogen Monoxide	0.9602	—	0.7874
Ethylene	0.9645	—	0.8224

Compressibility of Gases — Deviations from the Boyle-Mariotte Law (Ruddle, *J. pr. Chem.* [2], ix. 30-47). If this law were true in all cases, the relation between the pressure and volume of a gas at constant temperature would be expressed by the equation $p v = \text{constant}$. But the experiments of Regnault and Natterer have shown that the true relation is

$$p v = \text{const.} + \phi(p),$$

ϕ being the symbol of a hitherto undetermined function, which may be either positive or negative. Regnault,* whose experiments were made at pressures up to 30 atmospheres, and at a temperature near 4° C., found that hydrogen exhibits a positive, whereas all other gases exhibit a negative deviation from Boyle's law. Natterer,† on the other hand, whose observations were extended to much higher pressures, found that the negative deviation of air, nitrogen, and carbon monoxide is converted at very high pressures into a positive deviation, which finally becomes greater than that of hydrogen, and is enormous even for the latter. To a pressure of 2790 atmospheres correspond the following condensations:

Hydrogen	Nitrogen	Air	Carbon Monoxide
$\frac{1}{1008}$	$\frac{1}{705}$	$\frac{1}{726}$	$\frac{1}{727}$

Now, according to the gas-theory of Krönig and Clausius (iii. 131), the conditions for the constitution of a perfect gas are: (1). That the attractive forces between the molecules must be infinitely small. (2). That the radius of the sphere of action of a molecule must be infinitely small as compared with the length of the mean path of the molecules. (3). That the time intervening between two successive collisions must be infinitely small as compared with that of the free movement of a molecule. This last condition implies another, viz. that the portion of its path along which a molecule is exposed to the repulsive action of other molecules must be infinitely small as compared with the length of the path of free movement. In all actually existing gases, however, the attractions between the molecules have a real, though extremely small value, and it is just to these residual attractive forces that the ordinary negative deviations from Boyle's law are generally attributed. If, however, the imperfections in a gas due to attraction are reduced to the smallest perceptible trace, there still remain two causes which may produce a sensible deviation from Boyle's law, viz.: (1). The radius of the sphere within which each molecule exerts an elastic repulsive action must have a certain though very small magnitude ϵ . (2). The interval of time between two successive collisions, and the depth to which the elasticity of the molecules gives way, may have, as compared with the time and the medium length of the path of free motion, a certain magnitude of the order ζ . Now according to the views of Clausius respecting the manner in which the molecules rebound after collision, each molecule may be regarded as fencing off round itself, by repulsive forces, a space of medium radius δ , whose middle point is the centre of gravity of this molecule. A sphere of radius 2δ is called by Clausius the sphere of action of the molecule, and the sphere of radius δ may be called its sphere of elasticity. For convenience of consideration, the molecules may be replaced by elastic spheres of the magnitude of the spheres of elasticity. Moreover, the repelling forces which produce the rebound probably increase very rapidly as the molecules approach one another, so that the spheres of elasticity may be regarded as *hard-elastic*. According to this, ζ should be a small magnitude compared with ϵ , and of the two deviations last-mentioned the first should predominate. At all events it may be supposed that at constant temperatures the elasticity of the molecules is not altered by the number of collisions which take place in the unit of time. So long, therefore, as the paths of the molecules are long enough, the spheres of elasticity at constant temperature may be regarded as incompressible spaces of invariable magnitude.

If, therefore, the pressure on a gas is altered, the change of volume thereby produced affects only the spaces between the spheres of elasticity, which of themselves fill a constant space k . For a gas in which no other cause of deviation from Boyle's law exists, we have therefore, if its volume under the unit of pressure be denoted by v ,

$$v = k + \frac{v_1 - k}{p},$$

or, writing a for $v_1 - k$:

$$vp = a + kp.$$

* 'Relation des expériences entreprises . . . pour déterminer les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur.' Paris, 1847, p. 271.
† *Wien. Acad. Ber.* v. 361; vi. 557; xii. 199; *Jahresb. f. Chem.* 1851, 59; 1854, 87.

Supposing now that in hydrogen the attractions between the molecules disappear so completely that, in the discussion of Regnault's observations, they may be left quite out of account; it will then follow that the deviations from Boyle's law exhibited by this gas are due to the circumstance that the spheres of elasticity of its molecules have a not quite imperceptible magnitude as compared with the entire space which it occupies. Accordingly, k is the space occupied by the spheres of elasticity in a given quantity of hydrogen; a the empty space contained between them at 4° and 1 meter pressure. The ratio $\frac{k}{a}$ is found, from Regnault's experiments, to have the mean value 0.0007: consequently,

At 4° and 1 meter pressure, the spheres of elasticity of Hydrogen occupy 0.0007 of the space contained between them,

$$\text{or, since } \frac{0.0007}{1.0007} \text{ is sensibly equal to } 0.0007,$$

at 4° and 1 meter pressure, the spheres of elasticity of Hydrogen occupy 0.0007 of its apparent volume.

As already observed, the radius of Clausius' spheres of action is double that of the spheres of elasticity: consequently the volume of the spheres of action is 8 times that of the spheres of elasticity. Now Clausius has shown that the radius of the spheres of action is to the mean length of path of the molecules as the space occupied by the spheres of action to the total volume of the gas. If then the mean length of the path be denoted by l , we have

$$\frac{2\delta}{l} = \frac{8k}{v}, \text{ or } \frac{\delta}{l} = \frac{4k}{v};$$

and the behaviour of hydrogen under pressure may be expressed thus:

In hydrogen at 4° and 1 meter pressure, the mean length of path of the molecules is equal to 358 times the radius of the spheres of elasticity.

The approximate value of k , determined as above, may perhaps appear to involve a certain amount of improbability, leading as it does by a very simple calculation to the conclusion that, at 4° and 1 atm. pressure, the mean distance between the molecules of hydrogen is about twenty times as great as the radius of the spheres of elasticity.

It is usual, however, for reasons which need not here be discussed, to regard the distances between the molecules as very great in comparison with the dimensions of the molecules themselves. What is meant by 'dimensions of the molecules' it is not very easy to say, unless we understand by it the dimensions of the spheres of elasticity, or something similar; in that case the number twenty may appear rather small. It is, however, large enough to satisfy the necessary conditions of the gaseous state, as shown by the entire calculation above given, and especially by the equation $vp = a + kp$; and moreover it is directly supported by the experiments of Natterer, which show that when hydrogen under a pressure of 1 atmosphere is compressed to $\frac{1}{1000}$ of its volume, it scarcely conforms any more to Boyle's law; whence it follows that, if the mean distances between the hydrogen molecules at one atmosphere are reduced to $\frac{1}{10}$, they become magnitudes of the same order as the dimensions within which the specific forces of the molecules are active.

The volume at the pressure of 1 atmosphere, being taken as 1, each pair of numbers given by Natterer for p and $\frac{1}{v}$, yields by calculation a corresponding value of $\frac{k}{v}$. These are given in the following table:

p	$\frac{1}{v}$	$\frac{k}{a}$	p	$\frac{1}{v}$	$\frac{k}{a}$
2790	1008	0,00083	775	538	0,00075
2689	998	0,00083	751	528	0,00075
2594	988	0,00082	728	518	0,00073
2505	978	0,00082	706	508	0,00073
2423	968	0,00082	685	498	0,00072
2347	958	0,00081	665	488	0,00072
2277	948	0,00081	646	478	0,00072
2213	938	0,00081	627	468	0,00071
2154	928	0,00081	608	458	0,00071
2098	918	0,00081	590	448	0,00071
2044	908	0,00081	573	438	0,00071
1995	898	0,00081	556	428	0,00071
1948	888	0,00081	539	418	0,00071
1904	878	0,00081	522	408	0,00070
1862	868	0,00081	505	398	0,00070
1821	858	0,00081	488	388	0,00069
1781	848	0,00081	471	378	0,00069
1741	838	0,00081	454	368	0,00068
1701	828	0,00081	438	358	0,00067
1662	818	0,00082	423	348	0,00067
1623	808	0,00082	408	338	0,00067
1584	798	0,00082	393	328	0,00067
1546	788	0,00081	379	318	0,00067
1508	778	0,00082	365	308	0,00067
1471	768	0,00082	352	298	0,00068
1434	758	0,00081	339	288	0,00068
1398	748	0,00080	326	278	0,00070
1362	738	0,00082	313	268	0,00071
1326	728	0,00082	300	258	0,00072
1292	718	0,00081	287	248	0,00072
1259	708	0,00081	274	238	0,00073
1226	698	0,00081	261	228	0,00073
1194	688	0,00080	246	218	0,00069
1164	678	0,00081	235	208	0,00073
1134	668	0,00081	222	198	0,00072
1104	658	0,00081	209	188	0,00071
1074	648	0,00080	196	178	0,00068
1044	638	0,00080	183	168	0,00065
1015	628	0,00080	170	158	0,00059
986	618	0,00079	158	148	0,00057
958	608	0,00079	146	138	0,00053
930	598	0,00079	134	128	0,00046
903	588	0,00078	123	118	0,00046
876	578	0,00077	111	108	0,00033
850	568	0,00077	100	98	0,00027
824	558	0,00076	89	88	0,00017
799	548	0,00075	78	78	0,00000

Natterer's unit of pressure is that of the atmosphere: the above values of $\frac{k}{a}$ may be reduced to the unit of 1 meter by dividing them by 0.760. The temperature at which his observations were made is not stated, and he appears to have regarded the difference between the actual height of the barometer and 0.760 m. as a quantity which might be neglected; but his results, as they stand, agree remarkably well with those of Regnault. At pressures below 170 atmospheres, the value of $\frac{k}{a}$ comes out less than that deducible from Regnault's observations, viz. 0.0007, a result which may probably be attributed to a want of delicacy in Natterer's apparatus. From 170 atmospheres upwards the values of $\frac{k}{a}$ become nearly constant, the mean value up to 700 atmospheres differing but slightly from 0.007. For the highest pressures the

value of $\frac{k}{a}$ slowly increases, a result quite in accordance with theory: for as the molecules are brought closer and closer together, the time during which they can exert a repellent action on each other increases in proportion to the time of unrestrained movement. The molecules are therefore subject to repulsion during a longer part of their course, behaving indeed as if they exerted a perceptibly repellent action on one another, even beyond their spheres of elasticity; that is to say, the function $\phi(p)$ ultimately increases faster than the pressure. Its increase, however, in the series above given is so small, that it may perhaps be best to neglect it, at least provisionally, and regard the molecules, even at very high pressures, as hard-elastic. For these reasons Budde thinks it justifiable to assume that the observations of Natterer and those of Regnault may be represented by the same equation:

$$v = a + kp$$

with the value $\frac{k}{a} = 0.0007$ up to 700 atmospheres; and that above as well as below 700 atmospheres, the behaviour of hydrogen may be explained in second approximation by the assumption that the spheres of elasticity of its molecules have a magnitude which is not quite evanescent.

It has been assumed that the deviations of the gas from Boyle's law are due exclusively to the repulsive forces of its molecules. This is the simplest assumption that can be made, but it is neither necessary nor very probable. A very small residue of attractive forces may also be still present in hydrogen. The magnitude $\phi(p)$ will in that case resolve itself into two summations, one positive, the other negative, and the value kp will represent the difference between the two. It is probable, however, that the negative and positive portions of the deviation increase according to different laws, as indeed is distinctly seen in the case of air and of carbon dioxide.

Since then $\frac{k}{a}$ remains very nearly constant up to a large number of atmospheres, it may be inferred that the negative deviation is not able to disturb the positive to any sensible amount, and that therefore it can be but small in proportion to the latter. The value 0.0007 for the ratio of the magnitude of the elasticity-spheres to the volume of the gas may therefore be somewhat too small, but it is at least approximately correct.

The cause which determines the deviation of hydrogen exists likewise in the case of the other gases, and in them also it must tend to produce a positive deviation. Moreover, it is not improbable that the heavier molecules of the other gases may possess spheres of elasticity larger than those of hydrogen, and that consequently there enters into their deviations a positive element which exceeds the total deviation of the latter. At low pressures, however, this property of the last-named bodies is disguised by the attraction of their molecules.

Under all circumstances the magnitude $\phi(p)$ has to be divided into parts, one of which, $\phi-$, is negative, and arises from the residues of attraction in the gas, while the other, $\phi+$, is positive. Under different pressures the following combinations occur:—

- (1.) p very small $\phi+ = \phi- = \frac{1}{\infty}$; nearly true for all gases.
- (2.) p moderately large $\phi+ > \phi-$. Case of hydrogen.
 $\phi- > \phi+$. Case of other gases.
- (3.) p very large $\phi+ > \phi-$. Case of the most difficultly condensable gases.

In the remarks made on p. 853, the elasticity-spheres of the molecules are regarded, in accordance with ordinary usage, as globes. These observations, however, remain equally valid when the elasticity-spheres are supposed to be of any other shape, and δ represents their mean radius, that is to say, the radius of a globe having the same volume as the spheres of elasticity.

Results in accordance with the preceding have been obtained by Hemilian, Mendelejeff, a. Bojuský (*Deut. Chem. Ges. Ber.* ix. 1312), whose experiments show that, under a diminution of pressure of 2,200 to 20 mm., air, carbon dioxide and sulphur dioxide exhibit both positive and negative deviations from Boyle's law; hydrogen, on the other hand, only positive deviations. Negative deviation, that is to say a compression greater than that which should take place according to Boyle's law, was observed in air, carbon dioxide and sulphur dioxide, under pressures exceeding 1 atmosphere; and positive in air between 20 and 650 mm., in carbon dioxide between 20 and 180 mm., in sulphur dioxide between 20 and 60 mm. Earlier experiments by Mendelejeff a. Kirpitschoff (*ibid.* vii. 486) also led to the conclusion that air at low pressures deviates considerably from Boyle's law, in the

positive direction, so that the product pv , if supposed = 1 at 250 mm., diminishes at 0.5 mm. to 0.6.

According to Amagat, on the contrary (*Ann. Chim. Phys.* [5], viii. 270), air under low pressures (6.5 to 10.5 mm.) conforms exactly with Boyle's law. The mean of forty-one series of experiments gave for $v > v'$ $\frac{pv}{p'v'} = 1.0014$; in thirty-six series the deviation from unity did not exceed 0.002.

Liquefaction and Solidification of Gases. Down to the year 1877, six gases, viz. hydrogen, oxygen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh-gas, had resisted all attempts to reduce them to the liquid or solid state; but towards the end of that year they were all liquefied by L. Caillietet (*Compt. rend.* lxxxv. 1016, 1213, 1217, 1270; *Ann. Chim. Phys.* [5], xv. 132-134); oxygen and hydrogen also by R. Pictet (*Compt. rend.* lxxxv. 1214, 1276; lxxxvi. 37, 106; *Chem. News*, xxxvii. 1. 83). The means adopted for the liquefaction of those gases were the same as those previously employed by Faraday in effecting the liquefaction of other gases, namely, cold and pressure, the gases being condensed in thick-walled tubes of fine bore by means of powerful forcing pumps capable of producing a pressure of 300 to 1,000 atmospheres, and at the same time subjected to the intense cold produced by means of liquid sulphur dioxide and solid carbon dioxide.

Oxygen.—Evidence of the liquefaction of this gas was first obtained by Caillietet, and his results were communicated to the Academy of Sciences at Paris on December 2, 1877. Under a pressure of 300 atmospheres, and at a temperature of -29° , produced by the evaporation of liquid sulphur dioxide in a current of dry air, the gas appeared to undergo no alteration, but on allowing it to expand by suddenly removing the pressure, whereby a great fall of temperature is produced, a fog was observed in the tube, indicating the liquefaction, and perhaps solidification of the oxygen.

Nearly at the same time, Pictet, by the use of more powerful apparatus, whereby the gas was subjected to a pressure of 320 atmospheres and cooled to -140° by the combined effects of the evaporation of liquid sulphur dioxide and carbon dioxide, succeeded in liquefying the gas in a long glass tube; and on opening a screw-tap at the end of this tube, a jet of liquid oxygen was seen to spirt out with extreme violence. Pieces of slightly ignited charcoal held in this jet inflamed spontaneously and burned with intense vividness. A ray of electric light thrown upon the jet showed that it was composed chiefly of two parts; a central portion some centimeters long, showing by its whiteness that it consisted of liquid or even of solid oxygen; and an exterior portion, the blue tint of which indicated the presence of oxygen compressed in the gaseous state. In a subsequent experiment, the presence of solid particles in the jet of liquid oxygen was confirmed by illuminating it with polarised light.

Hydrogen.—Dry hydrogen, obtained by decomposing potassium formate with potassium hydroxide, was subjected to a pressure of 650 atmospheres and a cold of about -140° . On opening the tap, liquid hydrogen escaped with violence, making a sharp hissing sound. The jet had a steel-blue colour, and was perfectly opaque for the length of 12 centimeters. At the same moment a rattling was heard like that made by hail when it falls upon the ground, and the hissing became transformed into a peculiar noise, resembling that made by a fragment of sodium thrown upon water. Almost immediately the jet became intermittent, and shocks were felt in the cock at each escape. During the first jet the pressure fell from 650 atmospheres to 370. After closing the tap, the pressure gradually fell for several minutes down to 215 atmospheres, and then slowly rose to 225, where it again became stationary. On re-opening the cock the jet issued in so intermittent a manner as to show that the congelation of hydrogen had taken place in the tube. This was demonstrated by the progressive escape of all the hydrogen when the pumps were stopped, and the production of cold arrested (Pictet). Evidence of the liquefaction of hydrogen was also obtained by Caillietet.

Nitrogen.—This gas, prepared by the action of copper and ammonia on atmospheric air, then washed and dried over melted potash and strong sulphuric acid, was subjected to a pressure of 300 atmospheres at $+13^{\circ}$. On allowing it suddenly to expand, the gas remaining in the tube condensed to a mass of very minute liquid drops, which gradually disappeared from the sides of the tube and collected in the axis in the form of a vertical column, this series of changes taking place in about three seconds. A similar result was obtained with dry air quite free from carbon dioxide (Caillietet).

Nitrogen Dioxide passes to the liquid state under a pressure of 104 atmospheres at -11° ; at $+8^{\circ}$ it remains gaseous under a pressure of 270 atmospheres (Caillietet).

Carbon Monoxide is liquefied under the same circumstances as oxygen, viz. by a pressure of about 300 atmospheres at -29° , and sudden expansion (Caillietot).

Methane, CH_4 , similarly treated (pressure and temperature not stated), likewise exhibited a misty appearance at the moment of expansion.

Acetylene, C_2H_2 , was liquefied and solidified by P. and A. Thénard in 1874, by the action of the silent electric discharge (p. 34 of this Supplement). Caillietot, on submitting it to strong pressure, found that it contracted in volume more rapidly than it should according to Boyle's law, and was ultimately converted into a transparent colourless liquid, the liquefaction taking place:

Under 48 atm. at $+1^{\circ}$	Under 83 atm. at 18°
" 50 " 2.5°	" 94 " 25°
" 63 " 10°	" 103 " 31°

On suddenly removing the pressure, the tube was filled with a white opaque mist.

GAS-LIQUOR. On the utilisation of Gas-liquor in the Ammonia-soda process, see Gerlach (*Dingl. pol. J.* cccxiii. 82; *Chem. Soc. Jour.* 1877 ii. 286).

GAS-WELLS. On the Gas-wells of Pennsylvania, see J. L. Smith (*Ann. Chim. Phys.* [5], viii. 566; *Chem. Soc. Jour.* 1877, i. 287). These wells give out enormous quantities of gas, which issues at very high pressure. The following are analyses of the gases from three of the wells:

	Burns Butler Co.	Lechburg Westmoreland Co.	Harvey Butler Co.
CO_2	0.34	0.35	0.66
CO	trace	0.26	—
H	6.10	4.79	13.50
CH_4	75.44	89.65	80.11
C_2H_4	18.12	4.39	5.72
Hydrocarbon, of composition not stated	—	0.56	—

The gas from the Delampter well, about 30 miles from Pittsburgh, consists chiefly of ethane, C_2H_6 .

GASTALDITE. This name is given by J. Strüver (*Jahrb. f. Min.* 1876, 664) to a mineral which occurs in chloritic slate in the Val d'Aosta, near Brozzo, and in the valley of Lucano, accompanied by copper pyrites, garnet, and apatite. It crystallises in the monoclinic system. Type prismatic, through ∞P and ∞R , the terminal faces being indistinct. It occurs also pulverulent and fibrous. Prismatic cleavage with an angle of $124^{\circ} 25'$. Fracture conchoidal. Hardness 6-7. Sp. gr. 3.041. Colour blackish-blue to sky-blue. Streak greyish-blue. Lustre vitreous to pearly. The plane of the optic axes is the plane of symmetry. Gastaldite exhibits negative double refraction, an inclined dispersion, and strong pleochroism. An analysis showed it to have the following percentage composition:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
58.55	21.40	9.04	3.92	2.03	4.77	trace = 99.71

from which the formula $3\text{RO} \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ is obtained: $\text{RO} = \text{FeO}, \text{Na}_2\text{O}, \text{MgO}, \text{CaO}$.

GASTRIC JUICE. Observations on the composition and physiological action of the gastric juice have been made by Ch. Richet (*Compt. rend.* lxxxiv. 450, 1514) on a patient upon whom, in consequence of the complete closure of the œsophagus, the operation of gastrotomy had been performed. Through the fistulous opening thus established, pure gastric juice, quite free from saliva, was obtained by washing out the stomach with distilled water, and then placing in the mouth some sapid substance which, by its reflex action, provoked a relatively abundant secretion. Pure gastric juice, thus obtained, is a colourless liquid, viscid, but easy to filter, having little odour and not putrefying spontaneously.

The mean acidity of the gastric juice, whether pure or mixed with food, is nearly equivalent to 1.7 gram of hydrochloric acid per 1000 grams of liquid. The acidity never fell below 0.5, nor rose higher than 3.2 grams. The quantity of liquid found in the stomach has no influence on its acidity, which, indeed, is almost invariable, whether the stomach be nearly empty or very full. Wine and alcohol increase the acidity, while cane-sugar diminishes it. If acid or alkaline liquids are injected into the stomach, the gastric juice re-assumes its normal acidity in about one hour. The gastric juice is more acid during digestion than when digestion is not proceeding, and the acidity increases towards the end of the operation of digestion.

Berthelot has shown (*Chem. Soc. Jour.* 1872, 783) that when an aqueous solution of organic and inorganic acids is shaken up with ether, the former dissolve in the

other while the latter remain for the most part undissolved. By following this method, Richet finds that the acids of the gastric juice are almost entirely inorganic, or, more strictly speaking, they are acids insoluble in ether.

Gastric juice, when left to itself, gradually ferments, the amount of organic acid slowly increasing at the same time, until it doubles that of the inorganic acid.

When the gastric juice is separated from the glands of the stomach and mixed with food, its acidity greatly increases during the artificial digestion thus set up, but the inorganic acids always predominate. The ferment producing this acidity is partially soluble.

The time required for digestion varies from three to four hours, for such aliments as starch, fat, or flesh proper: the digestion of milk lasts only about an hour and a half to two hours, while alcohol and water are still more rapidly absorbed, no trace of them being left at the end of thirty-five to forty-five minutes.

GAULTHERIA OIL. *Testing for Adulterations.*—The presence of sassafras oil may be detected by adding 3 or 4 drops of nitric acid (sp. gr. 1·3 to 1·4) to 4 or 5 drops of the oil. Pure gaultheria oil, thus treated, shows no change at first, but solidifies after some hours to a mass of colourless crystals (nitro-methylsalicylic acid); sassafras oil, on the other hand, assumes a blood-red colour, and soon changes to a brown amorphous mass. Chloroform may be detected by its odour when the liquid is warmed (*Chem. Centr.* 1876, 30).

GAULTHERYLENE, $C^{10}H^{16}$. This hydrocarbon boils at 160° , and has a vapour-density = 4·74 (referred to air). By oxidation with chromic acid mixture it is converted into a resinous mass. Hydrochloric acid gas is abundantly absorbed by it, and the product, after repeated rectification, boils at 185° . The distillate is colourless and has a camphorous odour (Biedermann, *Deut. Chem. Ges. Ber.* 1875, 1677).

GEHLENITE. This mineral occurs at Orawicza in the Bannat, in round green lumps, enclosing granules of vesuvianite, and covered with a soft amorphous crust having the composition of samoite in which the alumina is partly replaced by ferric oxide. Analyses 1 and 2. Outer layer, of the gehlenite, sp. gr. 2·997 (Janovsky, *Deut. Chem. Ges. Ber.* vi. 1454). 3. Innermost layer of the rounded lumps, consisting of pure gehlenite, sp. gr. 3·01 (Janovsky and v. Zepharovich, *ibid.* vii. 109; *Wien. Akad. Ber.* [1 Abth.] lxxix. 26). 4. Vesuvianite. 5 and 6. Outer crust.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	K_2O	H_2O
(1).	32·39	18·53	1·25	3·61	6·65	—	0·51 = 100·63
(2).	32·55	undetermined	3·70*	andet.	6·52	—	undet.
(3).	30·73	22·24	0·41	3·01	37·93	6·10	0·37 = 100·79
(4).	36·31	23·36	2·90	0·51	25·32	5·19	3·35 = 99·15
(5).	27·98	30·23	8·51	—	3·76†	0·55‡	— = 100·39
(6).	28·17	undet.	8·33	undetermined	—	—	29·51

* Check determinations gave 3·42 and 3·56.

† $CaCO_3$.

‡ $MgCO_3$.

GELSEMIUM. From an examination of the constituents of *Gelsemium semper-virens* by Ch. Robbin, reported by Sonnenschein (*Deut. Chem. Ges. Ber.* ix. 1182), it appears that the substance called *gelsemic acid* by Wormley (2nd Suppl. 552) is identical with *æsculin*.

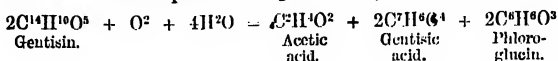
The alkaloïd gelsemine is an amorphous, colourless, or slightly pinkish mass melting below 100° to a colourless liquid. It dissolves but sparingly in water, more readily in alcohol, and freely in ether and chloroform. Its solution has a very bitter taste, and a strongly alkaline reaction. Its *hydrochloride* is amorphous, neutral, readily soluble in water, and the solution is precipitated by tannic acid, solution of iodine in potassium iodide, gold chloride, phosphomolybdic acid, &c. Platinic chloride produces an amorphous, lemon-yellow precipitate, which dissolves on warming, and crystallises on spontaneous evaporation in transparent quadratic octohedrons, which, on the addition of water, are changed into the amorphous compound, while platinic chloride goes into solution.

The composition of gelsemine is $C^{11}H^{13}NO_2$; that of the hydrochloride ($C^{11}H^{13}NO_2 \cdot 2HCl$), and of the amorphous platinum-salt $2[(C^{11}H^{13}NO_2 \cdot 2HCl) + PtCl_4]$. The pure alkaloïd dissolves in concentrated nitric acid, with a greenish-yellow, and in sulphuric acid with the same colour, which, however, soon changes into a reddish-brown and dirty red. When potassium dichromate is added to the sulphuric acid solution, the liquid changes first into cherry-red, and then into bluish-green; with cerosuccinic oxide a bright cherry-red colour is produced. A large pigeon, to which 0·012 gram of the hydrochloride was administered, died with convulsions in thirty-six minutes, and frogs exhibited the same symptoms.

GENTIAN. According to Hager (*Chem. Centr.* 1876, 823), some kinds of gentian-root contain tannin, whereas others do not. Villo (*Pharm. J. Trans.* [3], viii. 182) finds that cold infusions of *Gentiana Burseri* contain tannin. The colouring principle, gentianin or gentisin, gives the tannin reactions distinctly, for which reason Villo proposes to call it *gentianotannic acid*. The bitter principle, *gentiopicrin*, does not give the reactions of tannin.

GENTISIN, $C^{14}H^{10}O^5$. This substance, the colouring matter of gentian-root—also called *gentianin*, *gentianic acid*, and *gentisic acid* (ii. 830)—has been further examined by Hlasiwetz & Habermann (*Deut. Chem. Ges. Ber.* vii. 652). According to these chemists, the potassium and sodium-derivatives contain $C^{14}H^9KO^5$ and $C^{14}H^9NaO^5$ respectively, and *acetyl-gentisin*, formed by the action of acetyl chloride on gentisin, has the composition $C^{14}H^8(C^2H^3O)^2O^5$.

By the action of melting potash, gentisin is resolved into acetic acid, phloroglucin, and an acid $C^8H^6O^4$, called *gentisic acid* by Hlasiwetz & Habermann, who state that it does not agree in its properties with protocatechuic, oxysalicyllic, dioxybenzoic, or hypogallie acid.* The decomposition is represented by the equation



Gentisic acid melts at 197° [oxysalicyllic acid at 196 – 197°], and when heated above its melting point is resolved into CO^2 and pyrogentisic acid, $C^6H^4O^2$, a compound said to differ from all the known dioxybenzenes, viz. pyrocatechin, resorcin and hydroquinone.

GERANIENE, $C^{10}H^{14}$. This hydrocarbon, obtained from geranium oil by the action of phosphorus pentachloride, is converted, by treatment with half the calculated quantity of iodine, into cymene, $C^{10}H^{14}$ (Oppenheim & Pfaff, *Deut. Chem. Ges. Ber.* vii. 625).

GILBERTITE. The gilbertite of the Saxon and Bohemian tin mines occurs in two varieties, differing considerably from one another.

(1). One of them is of greenish-white to yellowish-white colour; translucent; occurs in crude lumps of compact to crystalline-granulo-laminar structure, vitreous to fatty lustre, hardness = 1, sp. gr. 2.65–2.72. It is found on all the veins of tin ore at Altenberg, Ehrenfriedersdorf, Geyer, Pöberschau, Zinnwald, and Schlaggenwald, alternating with tin-stone, wolframite, molybdenite, fluor-spar, &c., and penetrating into all the interstices of the tin-stone and wolframite. It is easily removed from these cavities when the lumps are broken up, and then always exhibits shining contact-faces, sometimes also impressions of the parallel streaks of the wolframite, and is even found imbedded in wolframite. It forms pseudomorphs after topaz, the substance of which has hitherto been designated as 'lithomarge,' having indeed considerable resemblance to many kaolins of the tin-stone veins, especially those of Altenberg, which formations have likewise been designated as lithomarge, or even as steatite. Kaolin may, however, be rubbed to dust, whereas gilbertite can only be broken into small laminae.

(2). The second variety, which is found in the same localities, accompanying apatite, iron spar, and nacrite, also tin-stone, wolframite, fluor-spar, &c., occurs in spherical and stellate, concentrically laminated modifications, also in six-sided tabular crystals commonly united in spherical groups. Colour light yellowish-green to sea-green and leek-green. Lustre, vitreous. Hardness = 3. Sp. gr. = 2.82. This variety is known as pseudomorphs after scheelite and apatite; it has also been found in roundish clusters, enclosed in lumps of siderite (from Schlaggenwald), which seems to suggest its production by transformation of that mineral.

The following are analyses of gilbertite from the localities above mentioned:—*a*, of the first variety from Ehrenfriedersdorf; *b*, of the same from Pöberschau; *c*, of the second variety from Ehrenfriedersdorf:—

	SiO ²	Al ² O ³	FeO	CaO	MgO	K ² O	Na ² O	F	H ² O	
<i>a.</i>	48.96	30.96	2.24	0.26	1.97	8.47	1.65	1.04	3.83	= 99.38
<i>b.</i>	48.10	32.30	3.30	0.43	1.12	10.02	—	0.81	4.09	= 100.14
<i>c.</i>	48.10	31.55	3.10	1.30	1.35	8.62	2.14	0.88	3.52	= 100.54

Lehmann found, in gilbertite from St. Austell in Cornwall, 45.15 SiO², 40.11 Al²O³, 2.43 FeO, 4.17 CaO, 1.90 MgO, and 4.25 water, whence Dana regards this Cornish

* The four known modifications of the acid $C^8H^6O^4$, or $C^8H^5(OH)^2CO^2H$, are [CO²H in 1], protocatechuic acid 1 : 3 : 4, oxysalicyllic acid 1 : 2 : 5, and two other dioxybenzoic acids, 1 : 2 : 4 and 1 : 3 : 6 (or 1 : 2 : 3) formed from the two corresponding disulphobenzoic acids (p. 289). The so-called *hypogallie acid* (ii. 239) has lately been shown by Beckett & Wright to be a mixture, most probably of opianic, hemipinic, and protocatechuic acids (see NARCOTINE).

variety as an impure kaolin. It is more probable, however, that in Lechunt's analysis the alumina was estimated too high and the potash overlooked.

Gilbertite is a distinct mineral species belonging to the mica group. The species 'lithomarge' may be abolished. Aluminic silicates of this class, which have not the composition of Gilbertite, are included in the formula, $Al^2O^3 \cdot 2SiO^2 + 2H^2O$, and consist either of nacrite or of kaolin. Such at least is the case with those which occur in Saxony: thus, the lithomarge of the tinstone veins, of the gangues of Freiberg, Johannsgorgenstadt, &c., of the pelosiderites (argillaceous sphærosiderites) of Zwickau, Würschnitz, &c., of the topaz-rock of Auerbach, &c., all consist either of nacrite or of kaolin. The amorphous varieties of lithomarge, called myelin and carnat, have also, as previously shown by Frenzel (*J. pr. Chem.* [2], v. 401), the composition of kaolin. Gilbertite and nacrite occur together on the tin veins, the formation of these two minerals appearing indeed to be related to that of the tin-ore gangues (Frenzel, *Jahrbuch f. Mineralogie*, 1873, 794).

GINGER. The extract obtained by boiling ground ginger (*Zingiber officinale*) with alcohol, and evaporating the filtrate, has a strong odour of ginger, and when heated in a current of steam yields a small quantity of essential oil lighter than water. When fused with soda, it yields protocatechuic acid (Stenhouse a. Groves, *Chem. Soc. J.* 1877, i. 553).

GINILSITE. A greyish-yellow mineral from the Ginil Alp, in Graubünden. Sp. gr. = 3.404. Composition:—

SiO^2	Al^2O^3	Fe^2O^3	CaO	MgO	H^2O
37.83	7.77	15.63	26.67	9.73	3.30 = 100.93

(Rammlersberg, *Jahrb. f. Min.* 1877, 97).

GISMONDIN. The gismondin of Salesl in Bohemia is rhombic, the crystals exhibiting a combination of the prisms with a brachydome and a macrodome. The type is quadratic and the crystals resemble those of bournonite. Axial ratio, $a : b : c = 0.99246 : 1 : 0.91897$. Of the zeolites occurring in the druses of Salesl, analcime is the oldest formation, natrolite the next, and gismondin the last. Gismondin often occurs in the place of apophyllite, which is also a younger formation than natrolite. The succession of the zeolites depends upon the degrees of solubility of their constituents, the more recent formations being the more soluble. The younger zeolite formations exhibit, with but slight variation in the amount of alumina, a decrease of alkalis and silica, and an increase of lime and water. With a constant proportion of silica, they are richer in water, and conversely, with equal proportions of water, they are poorer in silica (Schrauf, *Jahrb. f. Min.* 1877, 944). Gismondin occurs also in the druses of the basalt of the Schiffenberg near Giessen, as a younger formation than phillipsite (A. Streng, *ibid.* 1874, 578).

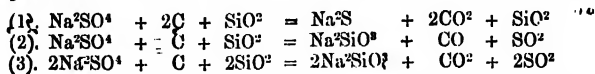
GLASS. *Constitution.*—From experiments by O. Schott (*Dingl. pol. J.* ccxvi. 346) it appears that ordinary glass is a mixture of amorphous alkali-silicate (or borate) with crystallisable calcium silicate. At the high temperature of the glass furnace, the sodium or potassium silicate dissolves the calcium silicate, and by its viscosity prevents the latter from crystallising out during cooling. The composition of glass may be represented by the general formula $\frac{xNa^2O}{yCaO} \cdot zSiO^2$. The proportions of the constituents for each kind of glass must be determined by considerations of utility. If the bases are in the ratio $Na^2O : CaO = 1 : 1$, the proportion of silica in the glass must not be less than 67 per cent.; otherwise devitrification is apt to take place during cooling. Glass thus composed may be represented by the formula $\frac{Na^2O}{CaO} \cdot 5SiO^2$.

With a larger proportion of sodium silicate the glass does not easily devitrify, even when the quantity of silica is less than 67 per cent.; for example, a glass having the composition $\frac{2Na^2O}{CaO} \cdot 4SiO^2$, and containing 57.1 per cent. silica, remains amorphous on cooling. For plate-glass, which is exposed to the weather, the proportion of silica should be as high as possible. Crown glass should contain less silica, but more lime. Its composition is usually 71.5 per cent. silica, 13.5 soda, and 15.0 lime.

Chemical Changes which take place during the Fusion of the Glass-mixture.—When the mixture consists simply of sodium carbonate, calcium carbonate and silica, the carbonates first fuse together, and are afterwards decomposed, at a higher temperature, by the silica, with evolution of carbon dioxide. But when, instead of sodium carbonate, a mixture of sodium sulphate and carbon is used, a more complex reaction takes place. When the pot is heated, the conduction of heat is at first so slow that even after exposure to a white heat for three or four hours, only the outer portions of the mass are fused, while the unfused portion in the centre is still sandy and

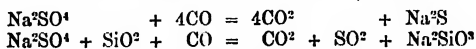
scarcely red-hot, and the fused glass near the edges of the pot remains turbid from admixture of unfused sand and small gas-bubbles. The zone between the solid centre and the fused outer portion is coloured brown by sodium sulphide, and still contains lumps of unaltered calcium carbonate. It is only in the second stage of the process, the 'refining,' that a rapid evolution of gas takes place.

Carbon and silica may act on sodium sulphate according to either of the three following equations:



In practice, for every molecule of sodium sulphate 0.6 of a molecule of carbon is used; this is too little for equation 2, but carbon from the furnace acts on the glass, and alkali (from 10 to 15 per cent.) volatilises:—0.6 mol. carbon is too much by 0.1 for equation 3; but the coke used contains 10 per cent. of ash, and some of it is burnt on the surface of the pot. The proportions in which the several ingredients enter into the mixture can therefore throw but little light on the reactions which take place.

The only gases actually given off are CO_2 and SO_2 ; nevertheless the source of these gases is not to be sought exclusively in the reaction represented by equation 3; for direct experiment shows that carbon monoxide, which should be evolved according to equation 2, acts upon sodium sulphate, either alone or in presence of silica, as follows:

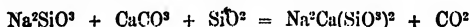


The sodium sulphide formed according to the first of these equations, acts further on the sulphate as follows:



A similar reducing action is perhaps exerted by the calcium sulphide in the soda-residues sometimes used in the manufacture of glass.

Lastly, the calcium carbonate in the glass mixture acts on the sodium silicate, forming calcio-sodic silicate, which constitutes the glass:



(O. Schott, *Dingl. pol. J.* cccv. 529; *Chem. Soc. J.* 1876, i. 121).

See also Frémy (*Compt. rend.* lxxxi. 1154; *Chem. Soc. J.* 1876, i. 787).

On the use of Soda-residues in glass-making, see R. Wagner (*Dingl. pol. J.* cccv. 358; *Jahresb. f. Chem.* 1865, 1085). On the utilisation of manganese-residues in the same manufacture, see *Jahresb. f. Chem.* 1873, 1042.

On the wear of the Melting-pots, and the best means of retarding it, see Platenka (*Dingl. pol. J.* cccxii. 322; *Jahresb. f. Chem.* 1876, 1117).

Formation of Gold-platinum Mirrors on Glass.—A plate of glass, having been well cleaned and polished, is covered with the following mixture, which is fused upon it at a red heat. A solution of 500 grams of platinum in aqua regia is diluted with 5 litres of water, and mixed with 2 kilograms of ammonia; the washed and dried precipitate is dissolved in 50 grams of hydrochloric and 50 grams of nitric acid; the solution is mixed with 50 grams of water; the whole is evaporated to dryness; and the residue is mixed with 2,000 grams of essence of lavender, 100 grams of turpentine oil, and 2.5 grams of sulphuretted turpentine-balsam. Secondly, 30 grams of gold are dissolved in aqua regia; the solution is evaporated to dryness; the residue shaken up with 500 c.c. water and 500 c.c. ether; the ethereal layer pipetted off and added to the platinum solution; and the ether evaporated. Lastly, to the mixed solution thus prepared is added an intimate mixture of 50 grams litharge, 50 lead borate, and 100 lavender oil; and the whole, after having been rendered homogeneous by shaking, is laid upon the glass (Dodé, *Deut. Chem. Ges. Ber.* i. 1273).

On the Etching of Glass with Hydrofluoric acid, see Heck (*Dingl. pol. J.* cccv. 129); Siegwart (*ibid.* cccx. 479); also *Jahresb. f. Chem.* 1875, 1094; 1876, 1117.

Coloration of Glass by Metals. Copper-ruby Glass. (Ebell, *Dingl. pol. J.* cccxiii. 53, 131, 212, 321, 401, 497; *Chem. Soc. J.* 1875, 485). Many metals, namely noble metals, such as gold and silver, and easily reducible metals like copper and lead, are capable of dissolving as such in melted glass. Gold, silver, and copper can enter as metals into glass in two molecular states, in one of which they do not colour the glass, while in the other they produce a strong coloration. The non-colouring molecular condition of the metals corresponds with the highest temperatures and the nascent state; the colouring molecular condition, with the lower temperatures

and the solid state of the metal. The passage from the former of these molecular states to the latter is called 'tempering' (*Anlaufen*).

Copper-ruby glass is prepared by two methods: 1. By coloration of the ready-made glass (*Lasur*). Copper and iron scales and ochre are rubbed with oil of turpentine to a thin paste, which is applied to the glass by a brush; and after drying, the glass is heated in the furnace, whereupon it absorbs a portion of the copper mixture and acquires a dark-green colour. The development of the ruby colour is effected by heating the copper in a muffle with wood-charcoal for a reducing agent. The coloration succeeds only with potash-glass free from lead, never with crystal or flint-glass.

2. *Fusion Process*.—The glass mixture and copper mixture are fused together and the fused mass is rapidly cooled, whereupon it appears colourless, or with a faint green colour due to iron or other accidental constituents; but on heating it further to the point at which it softens, the deep red colour is suddenly developed throughout the mass (*Anlauffarbe*). This change exactly resembles that which is observed in the development of the colour in gold-ruby glass (*2nd Suppl.* 555).

Solutions of the above-mentioned metals in glass obtained by fusion, solidify unaltered when quickly cooled; but on leaving them to cool slowly, the metal separates out, always in the metallic state, either as a finely divided precipitate, or in crystals, microscopic or macroscopic according to circumstances.

Gold, silver, and copper, either in the solid state or in solution, exhibit in their optical relations a very close resemblance to colouring matters of mineral or of organic origin, such as Prussian blue, indigo, the aniline-dyes, murexid, &c. Many colouring matters, indeed, have in the solid state a decided metallic lustre, and when finely divided or dissolved, a peculiar rich and bright colour, the two colours thus exhibited being nearly complementary to each other. A similar relation exists between the colours exhibited by gold, silver, and copper in the metallic state, and when dissolved in glass. These metals, indeed, in the state of igneous fusion, are true colouring matters, far exceeding the ordinary dye-stuffs in the solid state in their density, and consequently in their power of reflecting light (Ebell).

Crystallisation of Metallic Oxides from Glass.—Glass at a full white heat dissolves large quantities of metallic oxides, and deposits them on slow cooling in the micro-crystalline state. The oxides in which this effect has been observed are stannic oxide, chromic oxide, manganese dioxide (dissolved as manganoso-manganic oxide), and alumina (Ebell, *Dingl. pol. J.* cxxx. 64, 156, 288).

Bottle-glass. The following table gives the mean results of a number of analyses of bottle-glass by H. Macagno (*Chem. News*, xxxviii. 5). The solubility in water was obtained by weighing the quantity of material dissolved by 5 litres of water in one hour from 100 grams of finely-pulverised glass; the corrosion-degree was ascertained by boiling 100 grams of the same powder for one hour with 5 litres of potassium bitartrate solution of 0.33 per cent., and estimating the quantity of tartaric acid neutralised:—

	Spec. grav.	Chem. comp. per cent.				Solubility in water	Corrosion degree
		K ² O+ Na ² O	CaO	Al ² O ³ + Fe ² O ³	SiO ²		
White glass (five samples)	2.453	14.51	8.22	1.92	75.34	2.617	2.020
Light green glass (three samples)	2.474	15.52	7.73	5.47	71.27	3.177	3.975
Common green glass (eleven samples)	2.570	10.92	15.10	10.34	63.56	2.600	3.202
Dark green glass (two samples)	2.674	3.38	26.58	10.53	58.59	1.270	1.275
Red-brown glass (six samples)	2.516	15.77	9.28	6.88	66.15	3.470	4.888
Yellow-brown glass (seven samples)	2.553	14.62	14.35	8.02	62.84	2.504	3.387

One specimen of red-brown glass contained a trace of manganese. All the samples contained magnesia; in the analyses, when in sufficient quantity to be estimated, it is included with the lime. It would seem from the table that the chemical composition of glass is no criterion for judging of its quality. The amount of base does not indi-

cate the resisting power to water or acids. The deep-green glass seems the best for wine-bottles; the light-green, red-brown, and yellow-brown glasses are the worst, being easily attacked by solution of potassium bitartrate.

Composition of Ancient Glass. By E. Peligot (*Compt. rend.* lxxxiii. 1129; *Ann. Chim. Phys.* [5], xiii. 271). The following results were obtained from various specimens of ancient glass:—

SiO ²	66.7	66.0	67.4	70.9	69.4	69.4
CaO	5.8	7.2	2.7	7.9	6.4	7.1
Al ² O ³ , Fe ² O ³ and MnO ²	2.8	3.0	5.1	4.5	2.9	2.8
K ² O and Na ² O	24.7	23.8	24.5	16.7	21.3	20.7
	100.0	100.0	100.0	100.0	100.0	100.0

Soda and potash generally occurred together, showing that the alkali was obtained from the ash of marine plants. The proportion of lime was only the half or the third of that now in use, in consequence of which the glass generally altered considerably on exposure to the air. Some very old specimens of glass were found to contain lead; one specimen of very heavy glass, weighing 1,000 grains to the cubic inch, contained nearly half its weight of lead oxide.

Decomposition of Glass. Ordinary soda-glass is decomposed by hot water much more easily than the potash-glass used for combustion-tubes. When distilled water is boiled in a flask fitted with two tubes bent downwards a little above the cork, one made of ordinary glass, the other of combustion-tubing, and the condensed water which drops from them is allowed to fall on a piece of delicate red litmus-paper, the water dropping from the soda-glass tube will colour the litmus distinctly blue, whereas that which drops from the tube of potash-glass will produce no effect (*Tollens, Deut. Chem. Ges. Ber.* ix. 1540).

Various pieces of old glass examined by De Luynes (*Compt. rend.* lxxxiv. 303), were found to be covered with scales containing nearly 80 per cent. silica, whereas the glass itself did not contain more than 68 per cent. The transparency of the glass was not diminished by this change.

Glass submitted to influences which decompose it very slowly, such as continued exposure to moisture, to exhalations from damp earth, or to ammoniacal or acid vapours, often becomes covered with a thin film or scale, which exhibits very remarkable phenomena of irisation. This effect may be imitated, and an adherent coating resembling mother-of-pearl produced, by submitting the glass, under the influence of heat and pressure, to the action of water containing 15 per cent. of hydrochloric acid (*Frémy a. Clémandot, Compt. rend.* lxxxiv. 209).

Devitrification.—From numerous analyses of silicates separated from devitrified glass, Benrath (*Dingl. pol. J.* cciii. 19) infers that ordinary devitrified glass is not formed of tri- or tetra-acid silicates, but that glass in its ordinary state is a solution of silica or other crystallisable bodies in a ground-mass (perhaps RO.2SiO²), and that in this, as in all other solutions, different temperatures correspond with different maximum-contents of dissolved substance. Glass, apparently homogeneous, is like a supersaturated solution suddenly solidified, and when it is softened, or when movements take place in the interior of the mass, the crystallisable constituents, viz. silica and feldspathic silicates, separate out. According to this view, the devitrification of glass is a change analogous to the separation of crystallised chromic oxide (chromaventurin), or to the turbidity which shows itself in milk- or alabaster-glass containing calcium phosphate or stannic oxide.

From analyses of three specimens of devitrified glass, and of the amorphous glass from the same samples, H. Schwartz (*Dingl. pol. J.* ccv. 422) infers that amorphous glass may be regarded as the true mother-liquor of the crystals. The sp. gr. of the crystals examined was 2.656 to 2.660, that of the amorphous glass 2.641 to 2.648. These samples, which were from the glass-works of Fr. Siemens at Dresden, contained from 5.22 to 6.87 per cent. of manganous oxide. The property of the manganous oxide to act as a flux, suggests the employment of manganiferous blast-furnace slags in glass-works. The manganese in these slags is usually in the form of sulphide, and the sulphur might easily be removed by the addition of sodium sulphate, according to the reaction:



Soda and manganous oxide would thus be disposable for the formation of silicates, while the sulphur would be got rid of (Schwartz).

The following analyses of devitrified glass, and of the corresponding amorphous glass, are given by H. Wieser (*Dingl. pol. J.* cciv. 390):

	SiO ²	Al ² O ³	FeO	CaO	MgO	MnO	K ² O	Na ² O	S
Amorphous .	77.08	2.08	0.22	5.77	trace	0.14	1.18	13.88	0.25 = 100.60
Crystallised .	76.73	1.01	0.57	5.37	3.41	0.33	7.15	7.77	0.02 = 99.36

According to these analyses, the crystallised glass contains somewhat less silica than the amorphous, and about the same quantity of lime; the crystallised glass also contains about six times as much potash as the amorphous, whereas the latter contains twice as much soda as the former. Henrivaux (*Bull. Soc. Chim.* [2], xix. 6) points out that these results are contradictory to those obtained by Pelouze, Clément, Bontemps, and others, who have shown that the amorphous glass always contains more alkali than the crystals, whereas the latter are richer in silica and in lime (*2nd Suppl.* 556). Bontemps, on the other hand (*Bull. Soc. Chim.* [2], xxi. 166), is more disposed to admit the correctness of Wiesner's results, and thinks that the subject requires further investigation.

The crystallisation-products in ordinary glass have also been examined by Schott (*Pogg. Ann.* clv. 422). Previous to the formation of crystals in the glass, a film is produced on the surface by volatilisation of the alkali, exhibiting at first the colours of thin plates, but afterwards becoming white and opaque. Beneath this film bubbles are formed by further volatilisation of the alkali, and it is from these that the crystallisation starts, at first in the form of imperfectly developed crystalline growths, which afterwards unite into compact crystals. The formation of the crystals consists essentially in a separation of the amorphous from the crystalline constituents of the glass. The crystals consist of calcium silicate. Schott also regards glass as analogous in constitution to a saline solution saturated at high temperatures, the alkali-silicate forming the solvent of the calcium silicate. As the temperature rises, the calcium silicate becomes more soluble, and when cooled to a certain point, it separates out. The solution of the calcium silicate in the sodium silicate easily passes, however, into the supersaturated state, and such is its condition in ordinary glass, and it is only when the glass is kept for a considerable time at a red heat that the molecules of the calcium silicate are able to unite together. In many glasses made from impure materials, the rhombic crystals of calcium silicate are accompanied by hexagonal crystals of alumina.

Moulded-Glass. In order that glass may be easily shaped by pressing it into a mould, without the necessity of heating the mould too strongly, it must be easily fusible, must not pass too quickly from the plastic to the solid state, and must be capable of softening quickly when heated before the mouth of the furnace. Formerly lead-crystal glass (ii. 841) was the only kind that fulfilled these conditions; thus a moulded glass analysed by Benrath (*Dingl. pol. J.* ccxviii. 275) contained 50.80 per cent. SiO², 0.14 Al²O³ (with Fe and Mn), 28.11 PbO, and 11.62 K²O. Such glass was, however, too dear for the purpose; and, moreover, the pressed vessels made from it, which are always thick-walled, are too heavy. The first step taken to remedy these defects was the substitution of soda for potash. An English moulded-glass of recent manufacture, and having a density of 2.874, was found by Benrath to contain 61.27 per cent. SiO², 0.68 Al²O³ (with Fe and Mn), 33.36 PbO, 1.05 CaO, 7.55 Na²O, and 7.07 K²O. This composition was obtained by melting together 300 pts. sand, 110 minium, 10 chalk, 70 soda and potash; other manufacturers have attained the same end by using baryta or lime instead of lead oxide. Thus Renault, in Maestricht, by working with a mixture of 300 pts. sand, 80 minium, 40 limestone, 40 whiterite, 80 potassium carbonate, and 10 nitre, obtained a glass having the composition:

SiO ²	PbO	CaO	BaO	K ² O
61.9	16.0	4.5	6.3	11.3 = 100

and a light moulded-glass of recent English manufacture, sp. gr. 2.524, gave by analysis:

SiO ²	SO ³	PbO	Fe ² O ³	BaO	CaO	Na ² O
74.19	0.28	0.86	0.58	5.16	2.88	17.02 = 100.97

American moulded beer-glasses were found by Caplan (*Dingl. pol. J.* ccxxvii. 509) to have the following composition:

SiO ²	Fe ² O ³	Al ² O ³	MnO	CaO	MgO	Na ² O and residue
75.00	0.19	0.11	0.38	5.18	0.52	18.62 = 100

According to A. Frank, the American glass is very fusible and has a density of 2.486.

Alabaster-, Milk-, Bone-, Cryolite-, and Opal-Glass. By M. Hodk (*Dingl. pol. J.* ccxiv. 623-628). The chief constituents of alabaster-glass are non-ferruginous sand and potash. The presence of sodium-salts should be avoided, as they tend to produce transparent easily fusible glass. Most recipes include 'burnt bones,' but

good alabaster glass can be produced without them. Borax increases the lustre and fusibility of the glass, but is not absolutely necessary. Powdered talc is also advantageous. Good results are obtained by taking 100 parts sand, 40 parts potash containing at least 95 per cent. of carbonate, 5 borax, and 5 talc. The potash may be reduced to 30 parts if a hot regenerative gas furnace be used.

Coloured glasses are obtained by adding, for turquoise, copper oxide and sulphate, or copper oxide with a little nitre; and for chrysoprase, uranium oxide with a little copper oxide. A gray violet colour is obtained by adding manganese oxide and Ceylonese graphite.

Milk- or Bone-glass is obtained by adding sufficient bone-ash or tin oxide. Of late bone-ash has often been replaced by burnt guano:

(a) 100 parts sand.		(b) 100 parts sand.	
30	„ bone-ash.	35	„ potash.
30	„ potash.	30	„ burnt guano.
5	„ borax.	3	„ nitro.
5	„ minium.	3	„ tin oxide.

Cryolite is now applied in Bohemian works to imitate imperfectly French and Belgian opal-glasses. The effect of cryolite depends mainly on its alumina. The fluorine, however, acts prejudicially, on account of the volatile compound which it forms with silica. Too much cryolite renders the glass too opaque, and the fluorine injures the pots and furnace. The following mixture yields a good glass:—100 parts sand, 20 parts cryolite, 12 parts soda, 4 parts sodium nitrate, 2 parts zinc or lead-oxide.

An analysis of Belgian opal-glass gave:

SiO ₂	PbO	K ₂ O	Al ₂ O ₃	K ₂ O
63.7	16.5	0.3	16.8	2.3 = 99.6.

Here the alumina gives opacity, whilst the large quantity of lead oxide tends to the durability of the finished objects. Experiment shows that 100 parts of finely powdered felspar free from iron, and 22 of pinium free from iron and copper, form a completely homogeneous, fusible mass, easily worked without decomposition. This glass in its properties closely approximates to the French and Belgian glass. Metallic oxides yield very rich colours with it. See further Ebell (*Dingl. pol. J.* ccxxv. 70 and 168; *Chem. Soc. Jour.* 1878, xxxiv. 97).

Hard or Toughened Glass. This kind of glass, discovered by De la Bastie in 1875, is prepared by heating ordinary glass to its softening point, then immersing it in a heated bath of oil, fat, wax, paraffin, resinous or bituminous substances, and cooling it quickly. A. Bauer (*Dingl. pol. J.* ccxv. 381) dips the glass into a bath of paraffin heated to 200°, then cools it quickly to a certain point, and afterwards gradually. The best kind of bath is, however, a steam-bath, as it is free from the danger of fire arising from the use of fat or oil baths, and may be regulated to any desired temperature by the use of saturated, unsaturated, or superheated steam.

Glass treated in this manner is so hard that it cannot be cut with a diamond, and has a density of 2.460–2.468, that of ordinary glass being 2.429–2.438. It does not differ in appearance from ordinary glass. Plates of it may be repeatedly thrown on the ground without fracture, and give out a peculiar ring; but if they do break, they crumble into a multitude of small angular fragments; and the same sudden disintegration sometimes takes place without any apparent cause. The tenacity of glass toughened in an oil-bath is said to be equal to 601 kilos., and of glass toughened in a steam-bath 700 to 1000 kilos. per square centimeter, whereas that of ordinary glass is only 220 kilos. Bottles of toughened glass have been found to stand a pressure of 52 atmospheres, whereas ordinary glass bottles of the same thickness stand only 39 atmospheres. De la Bastie (*Dingl. pol. J.* ccxx. 186) found that a plate of hard glass 6 mm. thick was broken into fragments by a weight of 100 grams let fall upon it from a height of 0.8 meter. A plate 3 mm. thick withstood the fall of the same weight from a height of 5 mm., but was broken into very small fragments when the weight fell upon it from a height of 5.75 mm. A strip of hard glass withstood the heat of a flame without cracking, and remained unaltered when dipped into cold water, and heated in the flame while still wet. Pilati (*ibid.* 187) found that blue hard glass had a sp. gr. = 2.522, hardness = 5, and contained 68 per cent. silica, 10 lime, 2 alumina, 17 alkalis, and 3 magnesium, iron, chlorine, and cobalt-compounds.

According to Luyens a. Feil (*Compt. rend.* lxxxi. 341), hard glass breaks in a similar manner to Rupert's drops. A disc of it may, however, be bored through in the centre without breaking. A square plate of hardened mirror-glass from St. Gobain

showed in polarised light a dark cross, the arms of which were parallel to the sides of the square. The plate could be sawn or cut, without breaking, in the direction of those arms, but not in any other.

The peculiar constitution of toughened glass is not very well understood, but there can be no doubt that its molecules are in a state of tension like those of Rupert's drops and unannealed glass in general. According to Bauer, the effect of the sudden cooling is to preserve the homogeneity of the glass; slow cooling may give occasion to a disintegration of the homogeneous mixture of silicates, which is less liable to take place when the mass is quickly cooled. Pocklington (*Pharm. J. Trans.* [3], vi. 5) infers from optical examination that the physical structure of hard glass is exactly the same as that of glass under strong pressure, and he attributes its peculiar properties to the fact that it consists of a layer of ordinary glass enclosed between two layers of rapidly cooled glass. The slightest disturbance at the surface of contact of the layers in these different states of tension, causes the glass to fall to powder. The glass, if very uniformly hardened, may be worked with a file wetted with oil of turpentine, and with proper precaution it may be polished on a stone. Hydrofluoric acid attacks the soft parts of the glass more strongly than the hard parts, so that wave-lines are produced on the surface, corresponding exactly with those which the glass exhibits in polarised light.

On Soluble Glass, containing Alkaline Bases only, see R. Meyer (*Dingl. pol. J.* cccxvii. 280; *Chem. Soc. Jour.* [1878], xxxiv. 534): E. Bell (*Dingl.* cccviii. 47, 160; *Chem. Soc. Jour.* xxxiv. 689, 768).

GLAUBERITE, $\text{SO}^4\text{Ca}.\text{SO}^4\text{Na}^2$ (ii. 845). From measurements of the crystals of Glauberite from Westeregeln, near Magdeburg, v. Zepharovich (*Jahrb. f. Min.* 1874, 543) deduces the axial ratio, $a : b : c = 1.2199 : 1 : 1.0275$; angle, $ac = 67^\circ 49' 10''$. W. Schimper (*ibid.* 1877, 401) describes glauberite crystals from Pendschab, where it occurs attached to cubes of rock-salt, in forms having exactly the habit of the crystals from Westeregeln. The forms observed were $0P$, $-P$ predominant; then ∞P and $\infty P\infty$, with well-developed faces; and sometimes $-P$, $2P\infty$, and $\frac{3}{2}P\infty$, but only very secondary. Laspeyres (*ibid.* 947) describes glauberite from Aranjuez occurring on nodules of grey clay in crystals not more than 20 mm. long, but colourless, not altered by exposure to the air, and with well-developed faces. Axes, $a : b : c = 1.220924 : 1 : 1.0270307$; angle $ac = 67^\circ 49' 33''$, agreeing nearly with the measurements of v. Zepharovich. The most frequent combination is $-P$, ∞P , $0P$, $\infty P\infty$, with $3P3$ and P secondarily.

GLAUCODOTE, or cobalt-arsenical-pyrites, is found at Hakausbö in large twin crystals, whose form fully coincides with the acontite of Breithaupt. The forms observed were ∞P , $\infty P\infty$, $P\infty$, $\frac{1}{2}P\infty$, $P\infty$, $2P\infty$, $P.P2$. Twins according to two laws, the first being 'the twin-plane a face of ∞P '; the second 'the twin-plane a face of $P\infty$.' As the angle between two faces of this form is $61^\circ 3'$, a trilling can grow having a hexagonal appearance.

A trilling of this mineral is to be seen at the British Museum (W. J. Lewis, *Jahrb. f. Min.* 1877, 300).

GLAUCOHYDROELLASIC ACID, $\text{C}^{11}\text{H}^{10}\text{O}^7$. An acid formed by the prolonged action of sodium-amalgam on ellagic acid (p. 731).

GLAUCONITE. This iron silicate, which occurs in nodules in the greensand of various localities, is, according to F. Anger (*Min. Mittheil.* 1875, 153), not amorphous, but possessed of double-refracting structure. F. Denalque (*Jahrb. f. Min.* 1875, 422) has analysed glauconite from Belgium, where it occurs widely diffused as glauconitic sand; he finds it to contain

SiO^2	Al^2O^3	Fe^2O^3	FeO	CaO	MgO	K^2O	Na^2O	H^2O
60.42	4.79	19.90	5.96	3.21	2.28	7.87	0.21	5.28 = 99.92

whence the formula $3\text{RO}.2\text{R}^2\text{O}^3.4\text{SiO}^2.3\text{H}^2\text{O}$, in which $\text{RO} = (\text{Fe}, \text{K}^2, \text{Ca}, \text{Mg}, \text{Na}^2)\text{O}$ and $\text{R}^2\text{O}^3 = (\text{Al}, \text{Fe})\text{O}^3$ (compare ii. 846: 1st Suppl. 636; 2nd Suppl. 556).

GLAUCOPHANE (also called *Wichtyn* v. 1038). This mineral, originally found in Finland, occurs also at Zermatt and in the island of Syra. The glaucophane of Zermatt has been examined by Bodewig (*Jahrb. f. Min.* 1876, 771), that from Syra by Luedcke (*ibid.* 778).

Glaucophane belongs to the hornblende family, and may be classed with arfvedsonite, achmite, and aegyrine. The crystals from Zermatt exhibit only the prismatic zone ∞P , $\infty P\infty$, $\infty R\infty$, the forms $0P$ and $+P$ occurring but seldom. Angle $\infty P : \infty P = 124^\circ 44'$. Cleavage very distinct parallel to ∞P , the angle being $124^\circ 30'$, which is that of hornblende. Hardness = 6.5, sp. gr. = 3.0907 (Bodewig);

3.101—3.113 (Lüdecke). The chief direction of elasticity (the second bisectrix) lies in the acute angle formed by the crystallographic axes a and c ; 4.24 for red light (lithium), 4.16 for yellow (sodium), 4.13 for green (thallium). The optic axes lie in the plane of symmetry. The optical characters are negative. The mineral is strongly pleochroic, and absorbs light. Before the blowpipe it melts to a greyish-white non-magnetic enamel.

The mean of two analyses by Bodewig of the Zermatt mineral gives the following values:

SiO^2	AlPO^2	Fe^2O^2	FeO	MgO	CaO	Na^2O	
57.81	12.03	2.17	5.78	13.07	2.20	7.33	= 100.39

whence the formula $\left\{ \begin{array}{l} \text{RSiO}^2 \\ \text{RSi}^2\text{O}^2 \end{array} \right\}$ in which $\text{R} = \text{Fe, Mg, Ca, Na}^2$, and $\text{R} = \text{Al, Fe}$.

An analysis of the glaucophane from Syra gave

SiO^2	AlPO^2	Fe^2O^2	FeO	MnO	MgO	CaO	Na^2O	
55.64	15.11	3.08	6.85	0.56	7.80	2.40	9.34	= 100.78

whence Lüdecke deduces the formula $3\text{Na}^2\text{SiO}^2.6\text{R}^2\text{SiO}^2.3\text{Al}^2\text{Si}^2\text{O}^2.\text{Fe}^2\text{Si}^2\text{O}^2$, in which $\text{R} = \text{Fe, Mn, Mg, CO}$.

Strüver's gastaldito (p. 858) is completely isomorphous with glaucophane, but contains a larger proportion of aluminium silicate, $\text{Al}^2\text{Si}^2\text{O}^2$ (Bodewig).

GLAUCOPHANE-ROCKS. Glaucophane occurs, similarly to hornblende, as a constituent of rocks. In the glaucophane eclogites of Syra, the smaragdite, which is an ordinary constituent of eclogites (p. 703), is replaced by glaucophane. Glaucophane-slate also occurs in Syra, together with mica-slate containing glaucophane as an accessory constituent.

Glaucophane-eclogite consists principally of glaucophane, omphacite and garnet, with muscovite and quartz as secondary constituents, and approaching nearly to the eclogites of von Drasche. The mica-slate is found in two modifications, one consisting of parallel layers of muscovite and quartz, with numerous glaucophane prisms and small garnets as accessories; the other is quartzose, consisting of many layers of quartz one meter thick, separated by thin films of muscovite, the accessories glaucophane and garnet being isolated. The *eclogite-mica-slate* unites the constituents of glaucophane-eclogite and mica-slate. It consists of thin parallel layers of muscovite enclosing ellipsoidal quartz-masses, together with glaucophane, omphacite and garnet. *Glaucophane-slate* was formerly described as a diathene-rock, but is now found to consist of parallel layers of glaucophane separated by white or greenish muscovite, with epidote and hematite as accessories. Viret described rocks intermediary between glaucophane-eclogite and glaucophane-slate (poor in mica), to which Lüdecke assigned the names omphacite-zoisite-gabbro and epidote-glaucophane. The first consists of omphacite and zoisite, has a granular structure, with talc, muscovite, epidote, tourmaline and calcite as accessories; the second is a granular mixture of epidote and glaucophane, with omphacite, zoisite and garnet as accessories. *Glaucophane-zoisite-omphacite rock* consists of the three minerals included in its name; there is also a slate having the same composition. *Smaragdite-chlorite rock* is a granular mixture of smaragdite and chlorite with glaucophane, epidote and garnet. The crystalline limestone which covers the mica-slate contains mica and glaucophane (Lüdecke).

GLUCIC ACID. From the experiments of Grote and Tollens (*Liebig's Annalen*, clxxv. 181) it appears that the acid thus named by Mulder (ii. 848) has no separate existence. His acid calcium glucate is identical with calcium levulinate, $\text{C}^6\text{H}^4\text{CaO}^2$ (see *LEVULINIC ACID*); and the other salts which he describes as calcium glucates appear to be derivatives of a carbohydrate, $\text{C}^6\text{H}^{10}\text{O}^2$, and to be formed by the action of caustic lime on dextrose.

GLUCINUM or BERYLLIUM. The atomic weight and specific heat of this metal are still under discussion. J. Emerson Reynolds (*Phil. Mag.* [5], iii. 38) has determined, by means of a very delicate alcohol-thermometer, the weight of glucinum which at 100° contains the same quantity of heat as 108 parts (1 atom) of silver. This weight he finds to be C^2 , which therefore, according to the law of Dulong and Petit—that the atomic weights of all bodies in the solid state contain the same quantities of heat—must be the atomic weight of glucinum; and since the equivalent number of glucinum is 4.6 (ii. 852), it follows that glucinum must be a dyad, its chloride being GCl^2 and oxide GO . This result is in accordance with the periodic law of the atomic weights of the elements (2nd Suppl. 462).

On the other hand, Nilson and Pettersson (*Deut. Chem. Ges. Ber.* xi. 381) have determined, by means of Bunsen's ice-calorimeter, the specific heat of glucinum

obtained by reducing the chloride with sodium in an iron cylinder. The metal thus prepared contained 87.09 per cent. of pure glucinum, the rest being made up of glucinum-oxide, iron, and silica. Corrections having been made for these impurities, the specific heat of the pure metal between 0° and 100° was found to be 0.4079, which is about two-thirds of that determined by Reynolds. According to this result, the atomic weight of glucinum should be $3 \times 4.6 = 13.8$, and the metal should be trivalent, the chloride being GCl_3 and the oxide G_2O_3 , as originally supposed by Berzelius.

With this atomic weight, however, it is difficult to assign to glucinum any place in the periodic series, and on this account Lothar-Meyer (*Deut. Chem. Ges. Ber.* xi. 576) considers it most probable that, if glucinum be really trivalent, its equivalent 4.6, determined by Awdejew (ii. 852) is too high, and that its atomic weight, instead of 13.8, should be between 11 and 11.15, giving it a place in Mendeleeff's table between boron and carbon. With this atomic weight it would form the first member of the aluminium group, separated by the regular difference of 16 from the next member, viz. aluminium (27.3). Boron, hitherto placed in the same column with aluminium (see table, 2nd Suppl. 463), would then form the first member of a special group, so that between the alkaline earth-group and the nitrogen-group there would in future be, not merely two, but at least three groups, headed respectively by boron, aluminium, and carbon.

Another point noticed by Lothar-Meyer as of some importance in deciding the question as to the atomic weight of glucinum is that the atomic heat of oxygen, if calculated from the difference between the atomic heat of trivalent glucinum and the molecular heat of its oxide, G_2O_3 , comes out equal to 2.5 instead of the usual value ranging from 3.5 to 4.8 (Kopp, *Liebig's Annalen*; 3rd Suppl. 290). This anomaly is unfavourable to the view which regards glucinum as a triad.

The glucinum prepared by Nilson a. Pettersson, which, as already observed, was contaminated with silica, iron, and glucinum oxide, formed prismatic crystals, partly microscopic, and having the colour and lustre of steel. Its sp. gr. at 9° was 8.9101, whence, by calculation, that of the pure metal was found to be 1.64. Glucinum is not altered by contact with the air, neither does it decompose water. It dissolves in dilute acids and in caustic alkalis, with evolution of hydrogen. It is not attacked by oxygen or sulphur even at a red heat, but burns when heated in chlorine.

Glucinum iodide, mixed in solution with an equivalent quantity of bismuth or antimony iodide, forms double salts which, when left to evaporate for a few days over sulphuric acid, are obtained in well-defined crystals having the form of elongated prisms; they are, however, so hygroscopic as to preclude the possibility of exact chemical or crystallographical examination. *Aluminium iodide* yields similar double salts, which, however, form tabular crystals (A. Welkow, *Deut. Chem. Ges. Ber.* vii. 803).

Glucinum Palladiosochloride, $\text{GCl}_3 \cdot \text{PdCl}_2 + 6\text{H}_2\text{O}$, is obtained in deep-brown, very hygroscopic tabular crystals, by leaving a mixture of the concentrated solutions of its constituent chlorides to evaporate over sulphuric acid. It is also formed, with evolution of chlorine, by heating a concentrated solution of glucinum palladiochloride, $\text{GCl}_3 \cdot \text{PdCl}_4$. It is soluble in water and in alcohol (Wolkow).

Glucinum Platinochloride, $\text{GCl}_3 \cdot \text{PtCl}_4$, crystallises with $8\text{H}_2\text{O}$, according to Marignac (*N. Arch. ph. nat.* 1870, 374), Wolkow (*Deut. Chem. Ges. Ber.* 1873, 1288), and Thomsen (*ibid.* 1874, 75), not with $9\text{H}_2\text{O}$, as formerly stated by Thomsen (2nd Suppl. 558). Marignac confirms the observation of Thomsen that the crystals belong to the quadrate system, and finds that the angle of the terminal edges of the octohedral crystals is equal to 115° . The constitution of this salt is regarded by Nilson (*Deut. Chem. Ges. Ber.* ix. 1056, 1142) as tending to show that glucinum is a dyad metal, inasmuch as metals of higher quantivalence do not appear to form normal, but only basic platino-chlorides, and the decidedly trivalent metals, such as bismuth, arsenic, and antimony are not known to form platinochlorides at all.

GLUCONIC ACID, $\text{C}_6\text{H}_{12}\text{O}_7$. This acid, which Hlasiwetz a. Habermann obtained by the action of chlorine-water on glucose- or on cane-sugar (2nd Suppl. 559) may also be produced, together with dextronic acid, by the action of bromine-water and silver oxide on starch. The product of the oxidation, saturated with calcium carbonate, yields calcium dextronate, and with barium carbonate, barium gluconate, which, on evaporation, dries up to a gummy mass, subsequently yielding acicular crystals. *Paramylum* treated in like manner, yields, on neutralisation with baryta, the barium salt of dextronic acid, and, with lime, a salt which, from its composition, solubility, and amount of crystallisation-water, appears to contain an acid isomeric with dextronic and gluconic acids. The free acids are obtained as sour colourless syrups, but gluconic acid may be subsequently crystallised. The acid from *paramylum* is converted by the action of bases, such as baryta, into dextronic acid, and the latter

by the further action of the base, appears to be transformed into gluconic acid (Habermann, *Liebigs Annalen*, clxxii. 11).

GLUCOSE. See SUGARS.

GLUTAMIC or **AMIDOGlutARIC ACID**, $C^5H^9NO^5 = CH(NH^2) \begin{matrix} \diagup CH^2.CO^2H \\ \diagdown CH^2.CO^2H \end{matrix}$. See GLUTARIC ACID under PYROTARTARIC ACIDS.

GLUTARIC or **OXYGLUTARIC ACID**, $C^5H^6O^5 = CH(OH)(CH^2.CO^2H)^2$. See PYROTARTARIC ACIDS.

GLUTARIC ACID. Syn. with NORMAL PYROTARTARIC ACID (*q.v.*)

GLUTIN. See PROTEIDS.

GLYCERAMINE (TRIMETHYL-), $C^6H^{15}NO^2 = C^3H^6(CH^2)^3NO^2$, is formed by heating monochlorhydrin with trimethylamine till the odour of the latter is no longer perceptible. On adding to the resulting liquid a concentrated solution of platinic chloride, and leaving it at rest, ammonium platinochloride separates out, and the liquid filtered from this precipitate and evaporated, yields a crystalline mass, whilst the mother liquor retains an uncrystallisable substance which is precipitated by alcohol, and appears to be the platinochloride of monomethyl-glyceramine. The crystalline mass, purified by pressure and recrystallisation, yields the *platinochloride of trimethyl-glyceramine*, $(C^6H^{15}NO^2.HCl)^2PtCl^4$, in orange-coloured tablets apparently belonging to the orthorhombic system. These crystals are soluble in water, either hot or cold, and the aqueous solution is not decomposed by boiling. They are insoluble in alcohol, and give off hydrochloric acid in a vacuum. The *hydrochloride*, obtained by decomposing the platinum-salt with hydrogen sulphide, is a colourless, syrupy liquid, which, when treated with silver oxide, yields the corresponding hydroxide (Hanriot, *Compt. rend.* lxxxvi. 1335).

GLYCERIC ACID, $C^3H^6O^4 = CH^2OH.CHOH.CO^2H$, or, according to Wislicenus, $CH^2OH-COH-CHOH$ (*2nd Suppl.* 719). According to E. Mulder (*Deut. Chem.* [—O—])

Ges. Ber. ix. 1902), this acid is best prepared by mixing 50 grams of glycerin (commercial) with 50 grams of water in a large glass tube, placing this in a collar, and adding, by means of a funnel reaching to the bottom, 50 grams of fuming nitric acid. After three or four days the contents of three such tubes are slowly evaporated on the water-bath down to about 270 grams, and the syrupy mass thus obtained is preserved in a flask allowing the escape of the gas, which is slowly given off. 1620 grams of the syrupy mass are next mixed with 11 litres of water in a tinned copper vessel, 2400 grams of white lead are gradually added, and the mixture is left to stand for a day. The vessel is then warmed, with constant stirring, to $61^\circ-65^\circ$, and kept at this temperature for two hours. The liquid is decanted and allowed to deposit crystals, the mother-liquor added to the solid mass, the water lost by evaporation replaced, and the operation repeated two or three times. The lead salt thus obtained is almost colourless, and, for ordinary purposes, need not be recrystallised.

When glyceric acid is distilled in a retort over an open flame, and the distillate is treated with hydrogen sulphide, an acid is obtained which crystallises in large colourless laminae, melts at 83° , and agrees in composition with the formula $C^3H^6O^4.2H^2O$. Its *barium salt* has the composition $C^3H^4BaO^4.3H^2O$ (Böttinger, *Deut. Chem. Ges. Ber.* x. 266).

Glycerates.—The *strontium salt*, $(C^3H^5O^4)^2Sr$, obtained by saturating the acid with strontium carbonate, separates after a while, on adding a little alcohol to the solution, in groups of crystals, nearly insoluble in cold, easily soluble in hot water. Alcohol precipitates it as a crystalline powder. The *magnesium salt*, $(C^3H^5O^4)^2Mg + 3H^2O$, separates from very concentrated solutions in stellate groups of small crystals, which quickly effloresce on exposure to the air. It dissolves very easily in cold water and with moderate facility in alcohol; becomes anhydrous at 100° . The *copper salt*, $(C^3H^5O^4)^2Cu$, prepared by boiling the lead salt with cupric sulphate, and purified by repeated crystallisation, has a fine sky-blue colour and brilliant lustre. It dissolves somewhat sparingly in cold, easily in hot water. By prolonged heating in moderately dilute solution, it is decomposed, with separation of cuprous oxide, and the liquid separated therefrom and concentrated over sulphuric acid, yields a verdigris green salt easily soluble in cold water and alcohol. Cupric glycerate is precipitated by alcohol from its concentrated aqueous solution in the form of a pale blue crystalline powder. The copper is not completely precipitated from it by potash. The *manganous salt*, $(C^3H^5O^4)^2Mn + 3H^2O$, prepared like the copper salt, forms small, hard, shining crystals, sometimes united in spherical groups. It dissolves in water and in dilute

alcohol. It gives off water on exposure to the air at ordinary temperatures, and more at 100° , the total loss then amounting to 1 mol. At a higher temperature it gives off $1\frac{1}{2}$ mol. more, and assumes a peach-blossom colour, and at 120° it begins to decompose. The solution of the peach-blossom coloured salt, $(C^3H^5O^4)^2Mn + \frac{1}{2}H^2O$, in a small quantity of water, yields, after a while, the blue crystals of the tri-hydrated salt (K. Garzaroli-Thurnalak, *Liebigs Annalen*, clxxxii. 190).

Glyceric Anhydride, $C^3H^4O^3$, separates from an aqueous solution of glyceric acid, evaporated at 100° and left at rest, in microscopic crystals, and on recrystallisation from water, in slender six-sided needles. It is insoluble in cold alcohol and in boiling ether, but dissolves in 647 parts of boiling water, by which, moreover, it is very slowly reconverted into the acid (Sokoloff, *Deut. Chem. Ges. Ber.* xi. 679).

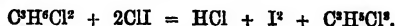
GLYCERIC ALDEHYDE, $C^3H^4O^3 = C^3H^3(OH)^2.CO^2H$ (A. Renard, *Compt. rend.* lxxxii. 562). This compound is formed by the action of electrolytic oxygen on glycerin suspended in dilute sulphuric acid. Hydrogen is evolved at the negative pole, and at the positive a mixture containing 3 per cent. CO^2 , 33 per cent. CO and 64 per cent. O; and on adding calcium carbonate to the liquid after forty-eight hours, to remove formic, acetic, and glyceric acids, then filtering, distilling, and leaving the distillate to evaporate over sulphuric acid, and drying, a white amorphous residue is obtained, consisting of hydrated glyceric aldehyde, $4C^3H^4O^3 + 11H^2O$, slightly soluble in water, nearly insoluble in alcohol and in ether, melting at 71° – 72° , boiling and subliming at 130° – 135° .

Glyceric aldehyde reduces ammoniacal silver nitrate, yields with oxidising agents (chromic acid, nitric acid, potassium permanganate, silver oxide) formic or acetic acid; by electrolysis, formic acid and a mixture of CO and CO^2 ; and when treated with sodium amalgam and water is apparently converted into glycerin.

When a solution of glyceric aldehyde is treated with ammonia, the mixture evaporated, and the dry residue repeatedly crystallised, crystals are obtained, very soluble in water, but insoluble in alcohol and in ether, and having the composition $C^3H^4N^2$. This compound sublimates at 120° – 130° without previous fusion, is reconverted into glyceric aldehyde by sulphuric or hydrochloric acid, but is not attacked by a boiling solution of sodium carbonate.

Glyceric Thioaldehyde, $C^3H^4S^2O.H^2O$, is formed by the action of hydrogen sulphide on a solution of glyceric aldehyde heated to 60° – 80° . It has a waxy appearance, melts at 80° – 82° , boils at 180° – 185° , dissolves sparingly in cold, very easily in hot water, but is insoluble in alcohol and ether (Renard).

GLYCERIN, $C^3H^8O^3 = C^3H^7(OH)^3$. *Synthesis*. Friedel and Silva (*Compt. rend.* lxxvi. 1594) have prepared glycerin synthetically from propylene chloride, obtained without the intervention of any allyl-compound or other derivative of glycerin itself. Propylene, C^3H^6 , prepared by converting acetone into pseudopropyl alcohol, and heating the latter with zinc chloride, was passed into a concentrated solution of iodine chloride; the propylene chloriodide thereby produced was suspended in water, and chlorine gas was passed into the liquid, till the iodine at first precipitated was redissolved; and the pure propylene chloride thereby obtained was heated in small quantities with dry iodine chloride to 140° in sealed tubes for eight hours, the tubes being opened after a while to allow the escape of hydrochloric acid, then sealed up, and again heated for eight hours to 140° . To remove the excess of iodine, the contents of the tubes were mixed with water, and chlorine passed into the liquid till the whole of the iodine was dissolved in the water as iodine chloride. The product (145.9 grams) separated from the water and dried, yielded on fractional distillation 18.8 grams of impure trichlorhydrin (boiling point 150 – 160°), containing about 50 per cent. of tetrachloropropane. The formation of the trichlorhydrin may be represented by the equation:



The impure trichlorhydrin heated with water to 180° yielded a small quantity of glycerin, which was recognised by conversion into acrolein and allyl iodide.

Properties.—The crystallisation of glycerin at low temperatures has already been mentioned (1st Suppl. 638). According to F. Nitzsche (*Dingl. pol. J.* ccix. 145), a method of obtaining glycerin in crystals was discovered by Kraut in 1870. This method (which is not described) is applied in the works of Sarg and Co. at Liesing, near Vienna, to the purification of glycerin, the crystals being freed from adhering mother-liquor in a centrifugal machine, then dried and melted. These crystals are described as monoclinic, absolutely colourless, having a pure sweet taste, very highly refractive, and melting at 20° to glycerin having a density of $30\frac{1}{2}$ Bm. According to V. von Lang, on the other hand (*Pogg. Ann.* clii. 637), these crystals are orthorhombic, with the axial ratio $a : b : c = 0.70 : 1 : 0.66$. They are very deliquescent.

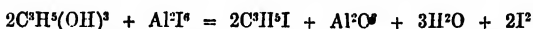
P. van Hamel Roos (*Chem. Soc. J.* 1876, i. 651) describes crystallised glycerin (56 lbs.) which appeared to have been solidified by the agitation of railway transport during the low temperature of January 1876. The crystals were monoclinic, colourless and had a pure sweet taste. On putting some of them into ordinary good glycerin, splendid crystals began to form, most of the impurities remaining in the mother-liquor. The crystals melted at 60° F., and the density of the liquid at this temperature was 1.261. According to A. Winkelmann (*Pogg. Ann.* cliii. 481), the density of glycerin is 1.220, and its specific heat 0.612. According to Oppenheim a. Salymann (*Deut. Chem. Ges. Ber.* vii. 1622), the corrected boiling point of glycerin under 755.55 mm. pressure is 200.08°.

Moderately concentrated glycerin heated to 150° burns with a blue flame, and may be burnt from a wick, without odour or residue (R. Godeffroy, *ibid.* 1566). E. Schering (*Dingl. pol. J.* ccxv. 287) observes that glycerin does not rise high in a wick. Its flame is colourless, and therefore well adapted for experiments on flame-coloration.

Reactions.—1. Glycerin heated with *zinc-dust* yields, together with an oil, a mixture of hydrogen and propylene, the bromide of which boils at 142° (Kerstein, *Deut. Chem. Ges. Ber.* ix. 695).

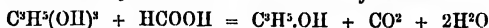
2. When glycerin is somewhat strongly heated for several hours with *sodium sulphide*, a liquid passes over, which, on fractional distillation, yields, together with products of higher boiling point, an ethereal liquid having an alliaceous odour, a density of 0.825 at 15°, and boiling at 58°. The alcoholic solution of this liquid is precipitated white by auric chloride and mercuric chloride, light yellow by silver nitrate, orange-yellow by lead acetate. It is violently attacked by nitric acid. Mercuric oxide dissolves in it, and on adding the oxide to saturation, the liquid separates into two layers, the lower of which solidifies to a crystalline mass. The crystals thus obtained dissolve easily in ether and in carbon bisulphide, and the compound crystallises from it in silky needles melting at 35° (Schlagdenhaufen, *Compt. rend.* lxxvi. 1021).

3. When glycerin is heated in a retort with *aluminium-foil* and *iodine*, the latter being gradually added, an oily liquid containing iodine passes over at 200°, and on washing this liquid with water, dissolving it in alcohol, and shaking the solution with mercury, a yellow mercury-alkyl iodide, C^3H^5HgI , is formed, which dissolves in warm alcohol, and separates therefrom, on cooling, in shining nearly white scales which quickly turn yellow. The alcohol from which the mercury-compound had separated gave no precipitate with water, thereby showing the absence of pseudopropyl iodide. The end-reaction of aluminium iodide with glycerin may therefore be represented by the equation:



analogous to that which represents the reaction of glycerin with phosphorus iodide (Hodgkinson, *Chem. News*, xxxv. 237).

4. Glycerin heated with *formic acid* is reduced to allyl-alcohol:

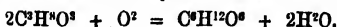


(Henninger, *Bull. Soc. Chim.* [2], xxi. 242).

5. When glycerin (2 pts.) is heated for some time to 120°–130° with *phenol* (2 pts.) and *sulphuric acid* (3 pts.), the mixture assumes first a yellow, then a yellowish-red, and finally a dark red colour; and on dissolving the thick mass after cooling in water, a brownish-yellow liquid is obtained from which hydrochloric acid throws down a colouring matter easily soluble in water and in alcohol, sparingly soluble in ether; it does not crystallise from these solutions. It is coloured a fine red by alkalis and by salts having an alkaline reaction, and forms lakes with baryta, alumina, lead oxide and other oxides. Heated with *aniline*, it is converted into a red colouring matter which acquires a violet-red tint when treated with ammonia. Similar bodies are obtained with *pyrogallol* and *thymol* (C. Reichl, *Deut. Chem. Ges. Ber.* ix. 1420).

6. **Conversion of Glycerin into Acetone.**—When dichlorodibromacetone, obtained by the action of bromine on dichlorhydrin (*2nd Suppl.* 14), is digested for several weeks at a temperature not exceeding 40° with water and granulated zinc, the action being assisted at first by addition of a little sulphuric acid and gentle heating, a liquid is obtained which, when distilled and dehydrated with calcium chloride, yields a acetone, together with a brominated compound. The acetone may be separated from the latter, by combination with sodium bisulphite. The reduction of the dichlorodibromacetone to acetone may also be effected by hydriodic acid (O. Lange, *Deut. Chem. Ges. Ber.* vi. 98).

7. **Conversion into Glucose.**—Glycerin is oxidised to glucose by the action of potassium permanganate in sunshine, or by chromic acid mixture:



Glycerin is also converted into glucose when placed in contact with iron which is undergoing oxidation by the action of air and water, the oxidising action being as it were transferred to the glycerin; and hog's lard similarly treated is resolved into fatty acid and glycerin, which is then oxidised to glucose (Kasman, *Bull. Soc. Chim.* [2], xxvii. 246).

8. *Fermentation*.—On the fermentation of glycerin induced by the action of schizomycetes, see p. 776.

Detection and Estimation of Glycerin.—When certain acid borates, common borax, for example, are dissolved in glycerin, the glycerin does not merely act as a solvent, but decomposes the borate, setting free a portion of the boric acid, which is then capable of imparting the well-known green colour to flame. This reaction may be used as a test for glycerin in water, wine, beer, milk, &c. The liquid is first made neutral or slightly alkaline (the presence of free acids would of course vitiate the test), and a borax bead is dipped into it, left at rest for a few minutes so as to allow solution to take place on its surface, and then held in the Bunsen flame in the usual way. Another and more delicate method is to place a little powdered borax on a watch-glass, pour on it some of the faintly alkaline solution, stir with a glass rod, and introduce some of the mixture into the flame by means of a looped platinum wire. In either case the green colour will appear more or less distinctly, if glycerin be present in sufficient quantity. The same reaction is produced by *erythrite*, and apparently also by *glycol*, but these compounds are not likely to be present in any liquid which is to be tested for glycerin. *Ammoniacal salts* have also the power of decomposing borax (*2nd Suppl.* 208), and must therefore be eliminated previous to the application of the test (Senier & Lowe, *Chem. Soc. J.* [1878], xxxiii. 438).

Estimation.—The amount of pure glycerin in commercial samples contaminated with ethers, fatty acids, &c., may be determined by treatment with a mixture of nitric and sulphuric acids, whereby the foreign substances are converted into soluble nitro-compounds, while the glycerin is converted into insoluble nitroglycerin, which may be washed with water, dried over the water-bath, and weighed. To facilitate the drying, the nitroglycerin is previously mixed with an equal weight of methyl-alcohol, the vapour of which easily carries off the water. 100 parts of pure glycerin dried in a vacuum at 120° – 150° yield 190 parts of nitro-glycerin (Champion & Pellet, *Bull. Soc. Chim.* [2], xix. 493).

For the estimation of glycerin in wine, Macagno (*Dingl. pol. J.* cxxvi. 95) digests a litre of the wine with recently precipitated lead hydroxide; evaporates the liquid on the water-bath, then adds a further quantity of lead hydroxide; exhausts the mass with absolute alcohol; and precipitates the dissolved lead by a stream of carbon dioxide. The filtered liquid when evaporated leaves nearly pure glycerin.

Metallic Glycerides (J. Puls, *J. pr. Chem.* xv. 83). Various metallic salts are dissolved by mixtures of glycerin and caustic alkali. When glycerin is mixed with *ferric chloride* and potash in certain proportions, a clear solution is formed, which, after a time, depending on the proportions of the mixture, suddenly begins to deposit ferric hydroxide, the precipitation going on till no more iron is left in the liquid. Strong solutions of this kind are of a cherry-red colour, and are only partially precipitated on heating; if dilute solutions, on the contrary, the precipitation is complete. Carbonic acid, in all cases, precipitates the iron completely; potassium sulphide also precipitates it, except in presence of a large excess of glycerin. These reactions are exhibited by all ferric salts, including the phosphate. When solutions from which the ferric oxide has been precipitated by heating, are evaporated to dryness, the residue dissolves completely in water, and the solution still retains the property of 'coagulating,' that is, depositing the iron as ferric hydroxide.

The facility with which this so-called coagulation takes place depends upon the proportions of the mixture. With glycerin, ferric oxide, and potash, in the molecular proportion $C^3H^5O^3 : Fe^2O^3 : KHO = 1 : 1 : 1$, no action takes place. With $3 : 1 : 1$ a solution is formed from which all the iron is precipitated by carbonic acid, or on dilution with water. The larger the proportion of glycerin, the more slowly does precipitation take place; with the proportion $6 : 1 : 1$ it takes place after two months only; and with $12 : 1 : 1$ no alteration is apparent even after five months. The proportion $3 : 2 : 1$ yielded a perfect solution, which, however, soon became gelatinous, and solidified so completely that it could be cut in pieces. With $3 : 2 : 2$ the solution remained complete for six hours; hence potash appears to retard the coagulation. With $3 : 8 : 1$ no iron is dissolved; $3 : 3 : 2$ gives a clear solution which immediately solidifies; so likewise with $3 : 3 : 4$ and $3 : 3 : 5$. With $3 : 4 : 3$ and $3 : 5 : 3$ no alteration was perceptible.

From these results Puls infers that the ferric hydroxide in these solutions is in

the so-called colloidal state. He finds, indeed, that solutions containing glycerin, ferric oxide, and potash in the proportion 3 : 1 : 1, and 79 per cent. water, which coagulated spontaneously after some time behaved towards reagents, as carbonate or chloride of potassium, &c., in the same manner as colloïd substances, being, in fact, suddenly brought by these reagents to the state of coagulation. The coagulation of the solutions employed in the experiments above described may therefore be attributed to the action of the potassium chloride which was present in all of them. The coagulation is also very quickly induced by sulphate, chlorate, nitrate, acetate, and tartrate of potassium, either in solution or in crystals; also by certain insoluble substances, as calc-spar, fluor-spar, witherite, and heavy-spar.

Uranium solutions and copper solutions react with glycerin and potash in the same manner as iron solutions. Experiments with cupric chloride showed that the solvent power of glycerin varies with the dilution of the liquid, as well as with the proportion of alkali. This is seen from the following tables:

TABLE I.

1 mol. glycerin and 1 mol. KOH	
When 100 pts. of the solution contain of glycerin :	92 pts. (1 mol.) glycerin dissolve :
0.19 pts.	7 pts. CuO
0.49 "	51.4 "
0.96 "	67.9 "
1.85 "	73.7 "
5.80 "	73.4 "

TABLE II.

1 mol. glycerin and 2 mol. KOH	
When 100 pts. of the solution contain of glycerin :	92 pts. (1 mol.) glycerin dissolve :
0.20 pts.	29.4 pts. CuO
0.51 "	65.4 "
0.72 "	71.6 "
0.96 "	71.4 "
1.80 "	73.6 "
2.56 "	74.7 "
4.47 "	75.8 "

TABLE III.

1 mol. glycerin and 3 mol. KOH	
When 100 pts. of the solution contain of glycerin :	92 pts. (1 mol.) glycerin dissolve :
0.20 pts.	47.7 pts. CuO
0.48 "	72.2 "
0.72 "	72.7 "
0.94 "	73.4 "
1.70 "	73.2 "
2.58 "	74.5 "
4.15 "	75.0 "
4.15 "	75.1 "

TABLE IV.

When 100 pts. of the solution contain of glycerin :	92 pts. (1 mol.) glycerin dissolve of CuO :	In presence of the following molecules of KHO :
0.19 pts.	7.0 pts.	1
0.20 "	29.4 "	2
0.20 "	47.7 "	3
0.20 "	53.9 "	4
0.20 "	59.9 "	6
0.20 "	64.6 "	8

In no case is the proportion of 79.3 pts. CuO (1 mol.) to 92 pts. glycerin (1 mol.) attained. It appears, however, from the first set of experiments (Table I.) that in a solution containing not less than 5.8 per cent. glycerin, 73 pts. CuO are dissolved for every 92 pts. glycerin present, so that the amount of glycerin contained in a liquid may be inferred from that of the cupric oxide dissolved by it; and this relation may be made available for the quantitative estimation of glycerin.

Bismuth solutions, mixed with glycerin and potash, exhibited reactions similar to the above, excepting that the quantity of bismuth held in solution was relatively much less.

Baryta, strontia, and lime, dissolved in proportions indicating the formulæ of the following compounds: $\text{BaO} \cdot 5\text{C}^2\text{H}^5\text{O}^2$ to $\text{BaO} \cdot 6\text{C}^2\text{H}^5\text{O}^2$; $\text{SrO} \cdot 10\text{C}^2\text{H}^5\text{O}^2$ to $\text{SrO} \cdot 20\text{C}^2\text{H}^5\text{O}^2$; $\text{CaO} \cdot 3\text{C}^2\text{H}^5\text{O}^2$ to $\text{CaO} \cdot 34\text{C}^2\text{H}^5\text{O}^2$.

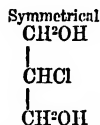
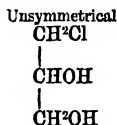
Sodium-glyceride, $\text{C}^3\text{H}_5(\text{ONa})(\text{OH})^2$, which Letts obtained by the action of sodium on glycerin (2nd Suppl. 564), crystallises from methyl alcohol in scales and nodules.

Its solution, mixed with cupric chloride, also dissolved in methyl alcohol, yields a green precipitate of a copper-glyceride containing cupric chloride.

Nitroglycerin, $C^3H^5(NO^2)_3O^2$. According to S. Kern (*Chem. News*, xxxi. 253), this substance explodes with maximum violence at 262° . At 187° it merely gives off red fumes, and at 204° a very slight explosion takes place.

The blasting oils of commerce are usually mixtures of trinitro-glycerin with the mono- and the dinitro-derivatives. For the analysis of these products, Ph. Hesse (*Zeitschr. anal. Chem.* 1874, 257) employs a modification of Dumas' combustion process, the mixture of the oil with cupric oxide being placed in a long combustion tube, and protected by a screen of tin plate during the expulsion of the air of the tube by the stream of carbon dioxide, and the combustion regulated as far as possible, so that the successive portions of the finely-divided blasting oil may be brought to the temperature required for combustion, only by the action of radiant heat. A simpler, and at the same time very exact method is to treat the blasting oil with alcoholic potash, whereby it is exactly decomposed into glycerin and potassium nitrate, in which the nitrogen may be estimated by the usual methods (Hesse). According to Sauer and Ador, on the other hand, (*Deut. Chem. Ges. Ber.* x. 1882), the amount of nitrogen obtained by this latter method is always too low. By Dumas' method they obtained from dynamite cartridges 18.35 to 18.52 per cent. nitrogen, answering to pure dinitro-glycerin, whereas by decomposition with alcoholic potash they obtained only 12.3, 12.5, and 13-14 per cent. nitrogen.

Chlorhydrins. 1. *Monochlorhydrin*, $C^3H^7ClO^2 = C^3H^5(OH)^2Cl$.—Of this compound there are two modifications, viz.:



Both these bodies are formed by heating glycerin with hydrochloric acid. The first, discovered by Berthelot in 1854 (i. 813), boils at 227° under ordinary pressure, at 139° under a pressure of 10 mm. of mercury, and is converted by nascent hydrogen into ordinary propyl glycol, $CH^2-CHOH-CH^2OH$. By treatment with potassium cyanide (exchange of Cl for CN) and subsequent saponification (O.OH for N), it is converted into an acid, $C^3H^5O^4$, having the constitution $CH^2OH-CHOH-CH^2-COOH$. This acid is a yellowish liquid which, when evaporated, appears to yield an anhydride analogous to lactide. Its salts crystallise with difficulty.

The second chlorhydrin occurs in small quantity amongst the higher-boiling portions of the product, and passes over on distillation in a vacuum between 145° and 160° . After rectification it boils at 146° under a pressure of 10 mm. It is probably identical with the compound which Henry obtained (*Deut. Chem. Ges. Ber.* vii. 409) by the action of hypochlorous acid on allyl alcohol, $CH^2=CH-CH^2OH + HOCl = CH^2OH-CHCl-CH^2OH$, and should be converted by nascent hydrogen into normal propyl glycol; but in all the reactions to which it has been subjected it yields a large quantity of polyglycerins (Hanriot, *Compt. rend.* lxxvi. 1139; *Bull. Soc. Chim.* [2], xxvii. 256).

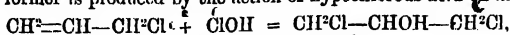
Monochlorethylin, $CH^2OH-CHCl-CH^2-OC^2H^5$, produced in like manner by the action of hypochlorous acid on ethyl allylate, is a thickish colourless liquid, of fruity odour and sharp taste, having a density of 1.117 at 11° , boiling at 183° .

Monochloracetin, $CH^2OH-CHCl-CH^2OC^2H^3O$, from ethyl acetate and hypochlorous acid, is a thick colourless liquid having a refreshing odour and bitter taste, a density of 1.27 at 9° and boiling at 230° .

Chlorobromhydrin, $CH^2OH-CHCl-CH^2Br$, from allyl bromide and hypochlorous acid, is a colourless liquid which turns brown on exposure to light, has a density of 1.764 at 9° , and boils at 197° ; and the isomeric compound, $CH^2OH-CHBr-CH^2Cl$, from allyl chloride and hypobromous acid, has a density of 1.759 at 11° , and likewise boils at 197° . When treated with nitric acid, it is converted, first into nitrochlorobromhydrin, $C^3H^5ClBrNO^3 = CH^2O(NO^2)-CHBr-CH^2Cl$, and then into a chlorobromopropionic acid, $CH^2Cl-CHBr-CO^2H$, which melts at 37° and boils at 216° . A third compound, isomeric with these, chlorobromhydrins, is the secondary alcohol, $CH^2Cl-CHOH-CH^2Br$, which Reiboul obtained by the action of hydrobromic acid on epichlorhydrin (ii. 808), (L. Henry, *Deut. Chem. Ges. Ber.* vii. 409, 757).

Dichlorhydrin, $C^3H^7Cl^2(OH)$, likewise admits of two modifications, one unsymmetrical and having the constitution of dichlorinated normal propyl alcohol,

$\text{CH}^2\text{Cl}-\text{CHCl}-\text{CH}^2\text{OH}$; the other symmetrical, and having the constitution of dichlorinated pseudopropyl alcohol, $\text{CH}^2\text{Cl}-\text{CHOH}-\text{CH}^2\text{Cl}$. The latter is the ordinary dichlorhydrin, which Berthelot obtained by heating glycerin with hydrochloric acid (i. 893); the former is produced by the action of hypochlorous acid on allyl chloride:



and appears also to be formed in small quantity in the preparation of ordinary dichlorhydrin (2nd Suppl. 317). The unsymmetrical modification is converted by oxidation into dichloropropionic acid, the symmetrical into dichloroacetone (Henry, *loc. cit.*)

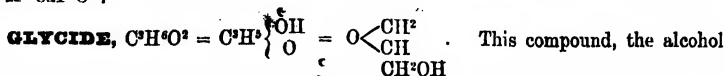
Epichlorhydrin and *Epicyanhydrin*, see pp. 734, 735.

Trinitrin or **Trinitropropane**, $\text{C}^3\text{H}_5(\text{NO}_2)^3$, is formed by distilling tripropylhydrin, (from allyl iodide) with silver nitrite. Treated with sodium, it yields a brownish product, which has not been obtained pure. Alcoholic potash converts trinitrin into a tripotassic salt which separates as a white powder, and may be purified by washing with alcohol or by recrystallisation from water. Trinitrin, treated with iron and acetic acid, is converted into glyceryl-triamine, $\text{C}^3\text{H}_5(\text{NH}_2)^3$ (Brackebusch, *Deut. Chem. Ges. Ber.* vi. 1289).

GLYCERYL OXIDE or **GLYCERYL ETHER**, $(\text{C}^3\text{H}_5)^2\text{O}^2$. This compound, which Linnemann a. von Zotta obtained by heating glycerin with calcium chloride (2nd Suppl. 565), has been further examined by v. Zotta (*Liebigs Annalen*, clxxiv. 87). To prepare it, glycerin (300 pts.) is distilled in a capacious retort with calcium chloride (45 pts.), previously dried by heating at 190° till the mixture becomes viscid and begins to froth over. The distillate is then cautiously heated over an open flame to remove volatile products, the residue is exhausted with ether, and the ether left to evaporate. The extract, subjected to fractional distillation, yields a liquid boiling between 160° and 210° , which, when shaken with strong potash-ley to remove phenol, leaves an oil which floats on the surface, and may be dried over potassium carbonate. The caustic potash solution also yields to ether a certain quantity of this oil, which, after evaporation of the ether, may be united to the first portion and rectified, whereby impure glyceryl oxide is obtained boiling between 168° and 175° . A further quantity may be obtained by similar treatment from the fractions of the crude product boiling between 150° and 280° . The whole may be purified by a few rectifications.

Glyceryl oxide is a colourless liquid, oily and nearly inodorous at ordinary temperatures, miscible in all proportions with ether, alcohol, and water, having a density of 1.16 and boiling at 171° – 173° . Heated with water in a sealed tube to 100° , it is converted into glycerin, and at 140° a brown substance is produced. With bromine it yields dibromhydrin, $\text{C}^3\text{H}_5\text{Br}^2(\text{OH})$. It is not attacked by sodium-amalgam. Heated with chromic acid mixture, it yields a distillate containing formic acid and acetaldehyde.

GLYCERYL-PHOSPHORIC ACID, $\text{C}^3\text{H}_5\text{PO}^6$. This acid, which was extracted by Gobley from brain and from yolk of eggs, and prepared by Pelouze by the action of phosphoric acid or anhydride on glycerin (ii. 891), has been further examined by Thudichum a. Kingzett (*Chem. Soc. J.* 1876, ii. 20), who prepare it by the action of boiling baryta-water on the brain-constituent, $\text{C}^{12}\text{H}^{18}\text{NPO}^3$, called by Thudichum *cephalin* or *kephalin*. On precipitating the resulting solution with alcohol, dissolving this precipitate in water, and evaporating on the water-bath, a barium salt was obtained having the composition $\text{C}^3\text{H}^7\text{BaPO}^6$. The precipitate formed by alcohol in the aqueous solution appears to contain both water and alcohol in combination; after washing with alcohol, it has the composition $\text{C}^3\text{H}^7\text{BaPO}^6 + \text{H}^2\text{O}$. The aqueous solution of the barium salt gives with lead acetate a precipitate of lead *glycerophosphate*, which, after drying, forms a hard, friable, faintly-coloured mass. The acid separated from it by hydrogen sulphide yields, on neutralisation with calcium carbonate and evaporation, a white calcium salt, $\text{C}^3\text{H}^7\text{CaPO}^6$; and on precipitating the mother-liquor of this salt with alcohol, an acid salt is obtained having the composition $\text{C}^6\text{H}^{16}\text{CaP}^2\text{O}^{12}$.



of the glycidic series (ii. 895), is prepared by heating epichlorhydrin, $\text{C}^3\text{H}^5\text{OCl}$, with potassium acetate, whereby glycidic acetate, $\text{C}^3\text{H}^5\text{O}(\text{OC}^2\text{H}^3\text{O})$, is obtained, as a mobile liquid having an ethereal odour and boiling at 168° – 169° , and treating this compound in ethereal solution with sodium hydroxide, whereby it is resolved into sodium acetate and glycide. This latter, when purified by fractional distillation, is a liquid boiling at 161° – 163° , and miscible in all proportions with water, alcohol, and ether. It unites with hydrochloric acid, and when heated with water is converted

into glycerin. Acid potassium sulphide converts it, by dehydration, into acrolein (H. v. Gegerfelt, *Bull. Soc. Chim.* [2], xxiii. 160).

GLYCOCHOLIC ACID. G. Hufner (*J. pr. Chem.* [2], x. 267) prepares this acid by covering fresh bile in a tall glass cylinder with a layer of ether, and adding 2 c.c. strong hydrochloric acid for every 50 c.c. of the bile. The whole then solidifies after a while to a crystalline pulp, which is drained on a filter, and the impure crystals of glycocholic acid which remain are crystallised from hot water.

GLYCOCINE. See GLYCOLLIC ACID, AMIDO- (p. 679).

GLYCODYSLYSIN, $C^{24}H^{38}NO^4$, is formed by heating glycocine with cholic acid to 190° – 200° , also by heating glycocholic acid to the same temperature. The product dissolves in alcohol, and separates therefrom as a white amorphous, chemically indifferent powder, easily soluble in alcohol, ether, and chloroform (J. Lang, *Bull. Soc. Chim.* [2], xxv. 180).

GLYCOGEN, $C^6H^{10}O^5$. *Occurrence and Formation in the Animal Organism.*—Experiments have been made by v. Mering (*Pflüger's Archiv. f. Physiologie*, xiv. 274) to decide the question whether (as supposed by Pavy, Dock, and others) glycogen is formed by direct transformation of bodies introduced into the system, or whether (as supposed by Tiffenbach and Weiss), these bodies merely contribute to the accumulation of glycogen in the liver by undergoing oxidation, and thus to a certain extent protecting and sparing the glycogen. The mode of experimenting consisted in introducing various substances into the system of rabbits and dogs, whose livers had been rendered as far as possible free from glycogen by previous starvation. The results showed that a considerable accumulation of glycogen in the liver is induced by the assimilation of grape-sugar, cane-sugar, milk-sugar, fruit-sugar, inulin, liech-nin, glycerin, arbutin, gelatin, and proteids (egg-albumin, fibrin, casein), whereas after the introduction of inosite, mannite, quercite, erythrite, and fats, no appreciable quantities of glycogen are found. These results seem to show that the formation of glycogen is a direct consequence of the transformation of certain substances introduced into the organism. The glycogen obtained after feeding with carbohydrates, meat and albuminoids was in all cases the same. J. Forster (*N. Rep. Pharm.* xxv. 733) found that in dogs which had been starved for several days, the quantity of glycogen in the liver was increased by the injection of sugar into the circulation, but by no means in proportion to the quantity of sugar thus introduced. He thence infers that the glycogen is produced, not directly from the sugar, but by the decomposition of albumin, and accumulates in the liver after the introduction of a considerable quantity of sugar into the circulation. The increase of glycogen produced by injection of sugar after prolonged fasting is a consequence of the accelerated decomposition of albumin thereby induced; and in accordance with this view it is found that the excretion of urea is at the same time considerably increased. S. Wolfberg (*Zeitschr. f. Biologie*, xii. 266; *Chem. Soc. J.* 1877, i. 484) also infers from his own experiments and those of Claude Bernard, Voit, Pettenkofer, Valentini, and others, that glycogen is an intermediate decomposition-product of albumin in the animal organism, the amount formed in any case being dependent on the quantity of albuminoids thus altered, and on the presence of various other substances, especially carbohydrates, which influence—by their greater or lesser power of resisting the decomposing actions of the organism—the rate at which the glycogen thus formed becomes further changed.

Glycogen occurs, together with glycocine, in the muscular tissue of the American scollop (*Pecten irradians*) (p. 879).

Transformation into Glucose.—It is commonly stated that glycogen is quickly and completely converted into glucose by the action of saliva and of pancreatic ferment. Siegon, however (*Chem. Centr.* 1877, 8), finds that, when the fermentation is completed, the glycogen-solution appears, from its power of reducing cupric oxide, to contain only a fraction of the quantity of glucose which it should contain, if the whole of the glycogen had been converted into that compound, viz. 34–41 per cent. under the influence of saliva, and 45–48 per cent. under that of pancreas extract. This shows either that the glycogen is converted, not into glucose, but into a substance which reduces cupric oxide in a different proportion, or that in the reaction above mentioned another product is formed besides glucose. Further experiments are required to decide which of these views is the correct one.

On the Estimation of Glycogen in the Liver, see Salomon (*Zeitschr. anal. Chem.* 1874, 470; *Jahresb. f. Chem.* 1874, 1054).

GLYCOGENIC ACID, $C^6H^{12}O^7$. An acid produced by treating an aqueous solution of glycogen at 100° with bromine, and then adding silver oxide: $C^6H^{10}O^5 + H^2O + Br^2 = C^6H^{12}O^7 + 2HBr$; and $C^6H^{12}O^7 + Ag^2O = 2AgBr + C^6H^{12}O^7$. It is an intensely sour syrupy liquid, the aqueous solution of which dissolves carbonates, forming salts

most of which are crystalline. The lead salt has the composition $C^8H^6Pb^2O^4$. In all the others the acid appears to be monobasic (Chittenden, *Liebig's Annalen*, clxxxii. 206).

GLYCOLINIC ACID. This name was given by Friedländer to an acid, $C^8H^4O^4$, which he supposed to be formed by the action of sodium-amalgam on an alcoholic solution of ethyl oxalate (1st Suppl. 640). According to Dobus, however, the only products of this reaction are glycollic, glyoxylic, and tartaric acids (2nd Suppl. 569).

GLYCOLIGNOSE. This substance, which J. Erdmann obtained as a residue from the wood of the spruce fir, after exhaustion with dilute acetic acid, alcohol and ether, and to which he assigned the formula $C^{30}H^{46}O^{21}$ (1st Suppl. 640), has been further examined by F. Bente (*Deut. Chem. Ges. Ber.* viii. 476), who obtains by analysis numbers agreeing with Erdmann's formula, but finds that when the glycolignose is boiled with hydrochloric acid, whereby, according to Erdmann, it is resolved into glucose and lignose, $C^{12}H^{20}O^{11}$, as shown by the equation, $C^{30}H^{46}O^{21} + 2H^2O = 2C^6H^{12}O^6 + C^{18}H^{28}O^{11}$, the insoluble residue of lignose which remains after washing successively with water, warm dilute ammonia, water and alcohol, amounts, not to 56.33 per cent. as required by the equation, or to 60–65 per cent. as actually found by Erdmann, but to 70.025 per cent. This residue also contains 0.54 per cent. carbon more than the amount required by theory, and the solution, which is turbid from separation of flocks, contains, not the required 48.51 per cent. of glucose, but only on the average 25.01 per cent. Pure grape-sugar similarly treated does not deposit any flocks. The lignose obtained as above gives, when fused with potash, oxalic and succinic acids, together with bodies resembling pyrocatechin, and probably containing protocatechuic acid, a result confirming Erdmann's statement that fir-wood contains aromatic compounds or residues. Bente doubts, however, whether glycolignose is a distinct chemical individual, inasmuch as it yields lignose in variable proportions, but not to the amount required by Erdmann's formula, even when subjected to the prolonged action of hydrochloric acid. *Poplar-wood* purified by Erdmann's method exhibited the same composition as fir-wood, and likewise yielded a quantity of lignose greater than that required by theory.

GLYCOLLIC ACID, $C^2H^2O^3 = CH_2OH.COOH$. *Formation.*—1. From dichlorethoxyl-ethylene by the action of water at 100° (p. 755). 2. By boiling monochloroacetonitril $C^2HCl(NO^2)N$, with milk of lime or caustic potash (Beckurts u. Otto, *Deut. Chem. Ges. Ber.* ix. 1591). 3. As ethylic ether, together with glyoxylic and tartaric ethers, by the action of sodium-amalgam on an alcoholic solution of ethyl oxalate (2nd Suppl. 569).

Preparation.—Fittig (*Ber.* ix. 1198) prepares glycollic acid by boiling a moderately strong aqueous solution of chloroacetic acid for a few hours, whereby it is completely resolved into hydrochloric and glycollic acids. On distilling the product and evaporating the residue on the water-bath, there remains a syrupy liquid containing only a trace of chlorine, from which it may be freed by again evaporating with water. The calcium salt obtained from the residue is pure glycollate.

Glycollic acid may also be easily prepared by heating aqueous oxalic acid with granulated zinc at 100° for a week, then filtering and adding excess of lime. The solution thus prepared contains calcium glycollate, together with a little glyoxylate, and the glycollate may be separated by removing the excess of lime with oxalic acid, boiling the liquid until the glyoxylate is destroyed, and concentrating by evaporation (Crommydis, *Bull. Soc. Chim.* [2], xxvii. 3).

Metallic Glycollates. The crystals of *calcium glycollate*, obtained in the manner just described, contain 5 mols. H^2O , one of which they lose on exposure to the air, and the other four at 100° , or over sulphuric acid in a vacuum (Crommydis). The existence of an anhydrous crystalline calcium glycollate observed by Fahlberg (2nd Suppl. 570) is confirmed by Carius (*J. pr. Chem.* [2], ix. 303). On evaporating the solution at a temperature as near as possible to 100° , this anhydrous salt separates on the surface in small crystalline groups, which sink to the bottom and form a hard crust. To obtain it pure, the supernatant liquid must be decanted while hot, and the crystals washed with a little water and dried. It is distinguished from the hydrated salt by its sparing solubility. If, on the other hand, the crystalline crust be left to cool in the liquid, the anhydrous salt becomes mixed with needles of the hydrated salt; and, lastly, if the solution be completely evaporated to dryness at 100° over the crystalline crust, there remains, together with the latter, a small portion of the salt in the form of an amorphous fissured mass, easily soluble in water. In Fahlberg's paper, above quoted, it is stated that hydrated calcium glycollate contains 2 mols. of water. Fittig, however, points out (*J. pr. Chem.* [2], x. 271) that this statement is incorrect, the error arising from a confusion between the old and new atomic weights

of calcium (20 and 40). The crystals contain 27-28 per cent. water, and this agrees with the formula $(C^2H^2O^2)_2Ca + 4H^2O$.

The following glycolates have been examined by G. Schreiber (*J. pr. Chem.* [2], xiii. 436). The *magnesium salt*, $C^2H^2MgO^2 + 2H^2O$, crystallises in extremely thin microscopic needles, and appears almost pulverulent when dry. 1 pt. of it dissolves in 12.6 pts. water at 18°; in boiling water it is much more soluble. The *strontium salt*, $C^2H^2SrO^2 + 5H^2O$, crystallises in slender microscopic needles; dissolves in 29.9 pts. water at 19°; is nearly insoluble in absolute alcohol; gives off the whole of its crystallisation-water at 180°. The *aluminium salt* is very soluble in water, and does not crystallise. The *silver salt*, contrary to the usual statements, was obtained in the anhydrous state, containing only 1.6 per cent. of hygroscopic water.

Chologlycollic acid, $C^2H^2O^2$, is formed by the action of nitrous acid on glycocholic acid (p. 456).

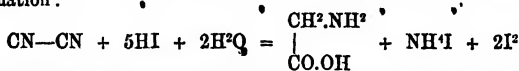
Diphenylene-glycollic acid, $C^{14}H^{10}O^2 = (C^6H^4)^2COOH-COOH$, is formed by the action of alkalis on phenanthrene-quinone (p. 676).

AMIDO-DERIVATIVES OF GLYCOLLIC ACID.

Amidoglycollic Acid, Glycoccine, or Glycine, $C^2H^2NO^2 = \begin{array}{c} CH^2.NH^2 \\ | \\ CO.OH \end{array}$.

Amidacetic acid.—This compound occurs to the amount of about 0.5 per cent., together with glycogen (2 to 2.4 per cent.) in the muscular tissue of the American scollop (*Pecten irradians*), found on the eastern coasts of the United States.

Formation.—1. From Cyanogen. When cyanogen gas is treated with concentrated hydriodic acid (sp. gr. 1.96) at the boiling heat, one of the cyanogen-atoms is converted, by assumption of hydrogen, into the methylamine-residue, CH^2NH^2 , whilst the second cyanogen-atom, by exchange of nitrogen for the elements of water, is transformed into carboxyl, the result being the formation of glycoccine, as shown by the following equation:



(Emmerling, *Deut. Chem. Ges. Ber.* vi. 1351).

2. By reduction of ethyl cyanocarbonate (p. 617).

3. Together with methylamine, ammonia, and carbon dioxide, when methyl-uric acid is heated for some time to 170° with hydrochloric acid saturated at 0° (H. Hill, *Sill. Am. J.* [3], xii. 428).

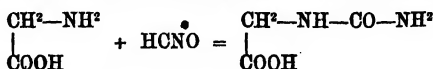
4. Together with tyrosine, ammonia, leucine, indol, and a viscid yellowish body, called gelatin-peptone—all, as well as the glycoccine, in small quantity only—by the pancreatic digestion of gelatin. The formation of glycoccine in the alimentary canal may explain, by its reaction with benzoic acid, the production of hippuric acid in the organism of vegetable-feeders; in carnivorous animals the glycoccine thus formed is converted into urea (Nencki, *ibid.* vii. 1593).

Reactions.—1. Glycoccine gives with *ferric chloride* a deep red colour, which disappears on addition of acids, and is regenerated by ammonia. On mixing a solution of glycoccine with a drop of *phenol* and a little *hypochlorous acid*, a fine blue colour is produced.

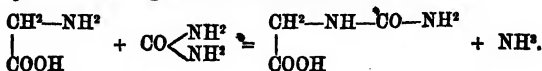
2. By oxidation with *ammonium permanganate* in presence of free ammonia, glycoccine yields oxalic, carbamic, and oxamic acids, and water; the formation of urea has not been observed (Drechsel, *J. pr. Chem.* [2], xii. 417).

3. Glycoccine, dissolved in nitric acid, is converted by *nitrous acid* into chologlycollic acid, $C^2H^2O^2$ (p. 436).

4. By *cyanic acid*, glycoccine is converted into hydantoic acid, thus:

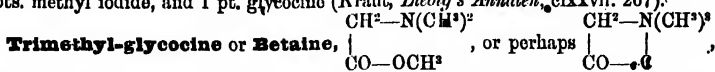


5. Hydantoic acid is also formed by boiling a solution of glycoccine and *urea* with excess of *baryta-water* as long as ammonia continues to be given off:



Sarcosine or *methyl-glycoccine*, treated in like manner, is converted into *methyl-hydantoic acid*.

Ethyl-glycocine, $C^2H^4(C^2H^3)NO^2$, is produced by treating glycocine with ethyl iodide and absolute alcohol. On agitating the product with silver chloride, the hydrochloride of ethyl-glycocine is obtained in needle-shaped crystals melting at 137° . Ethyl-glycocine is likewise found amongst the products of the reaction of 4 pts. alcohol, 2 pts. methyl iodide, and 1 pt. glycocine (Kraut, *Liebig's Annalen*, clxxvii. 267).

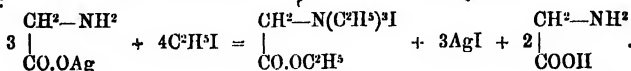


is formed by the action of methyl iodide (3 mol.) on glycocine (1 mol.); and the analogous compound, triethyl-glycocine, by heating triethylamine with ethylic chloracetate (p. 323).

Iodotriethyl-glycocine Ethylate or Ethylic Iodotriethylamidoglycollate, $CH^2-N(C^2H^5)^3I$

(Kraut, *Liebig's Annalen*, clxxxii. 172). This ether is formed

by the action of ethyl iodide (4 mol.) on silver glycocine (3 mol.) at ordinary temperatures:



The hard crystalline crust which forms after a few days is to be washed, first with cold alcohol, then with cold water. The ethylic iodotriethylamidoglycollate is found in the alcoholic extract. The corresponding platinochloride, $[Cl(C^2H^5)^3N.CH^2.COOC^2H^5]^2PtCl^4$, crystallises in thick orange-coloured anhydrous crystals which are soluble in water. The mother-liquor of this salt contains glycocine and diethyl-glycocine. The aqueous extract contains two-thirds of the glycocine employed in the reaction. The residue insoluble in alcohol and in ether still contains, together with ethyl iodide, a portion of the ethylic iodotriethylamidoglycollate, which, when boiled with an alkaline hydroxide, passes into solution, with separation of alcohol.

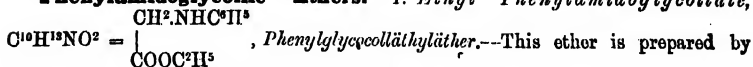
Chlorotriethylglycocinaminonium platinochloride, $[Cl(C^2H^5)^3N.CH^2.COOH]^2PtCl^4 + 2H^2O$, crystallises in roseate, well-defined monoclinic crystals, which are nearly insoluble in alcohol, and give off their water at 100° .

Diethylglycocine Ethylate or Ethylic Diethylamidoglycollate, $C^2H^{10}NO^2 = CH^2.N(C^2H^5)^2$, is obtained by distilling silver-glycocine with ethyl iodide, not in excess, $CO.OC^2H^5$

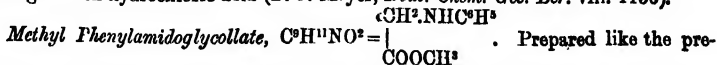
after the two substances have been left in contact at the temperature of the air for several days. It is a colourless alkaline liquid having a density of 0.919 at 15° and boiling at 174° . The corresponding platinochloride is at first oily, but solidifies after a while in short monoclinic anhydrous crystals. This ether, heated for some hours with ethyl iodide, is converted into iodotriethylglycocinaminonium ethylate.

Silver-glycocine, treated in like manner with methyl iodide in excess, yields the methylic ether of trimethyl-glycocine or oxynourine, and oxynourine or betaine itself, both of which are found in the alcoholic extract of the product (Kraut).

Phenylamidoglycollic Ethers. 1. *Ethyl Phenylamidoglycollate*,



heating 1 mol. ethylmonochloracetate with exactly 2 mol. aniline over an open flame till reaction begins, then removing the source of heat, and allowing the reaction to go on quietly to the end. The whole then solidifies to a crystalline mass, which may be freed from aniline hydrochloride by boiling with water. On dissolving the residual oil in alcohol, and adding water by drops to the cooled solution, a solid body is precipitated; and after these operations have been several times repeated, ethyl phenylamidoglycollate is obtained in colourless nacreous laminae, melting at 57° – 58° , only slightly soluble in water even when hot, but dissolving with moderate facility in cold alcohol and ether, very easily in the same liquids when hot, also in hydrochloric acid. It is therefore advisable, in preparing this body, to use a slight excess of the chloroacetic ether, in order to avoid the presence of free aniline, and the necessity of removing it with hydrochloric acid (P. J. Meyer, *Deut. Chem. Ges. Ber.* viii. 1156).

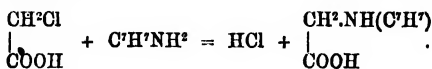


ceding. The viscid oil obtained by heating 1 mol. methyl chloracetate with 2 mol. aniline at once yields crystals of aniline hydrochloride, which may be removed by

agitation with water. By distilling the residual oil in a current of steam, a turbid distillate is obtained, which soon deposits the methylic phenylamidoglycollate in splendidly iridescent needles and prisms which may be purified by redistillation. They melt at 48° , are nearly insoluble in water, but dissolve easily in alcohol, ether, and hydrochloric acid (Meyer, *ibid.* 1157).

Tolylamidoglycollic acid or **Tolylglycocine**, $\text{C}^6\text{H}^{11}\text{NO}_2 = \begin{array}{c} \text{CH}_2\text{NH}(\text{C}^6\text{H}_7) \\ | \\ \text{COOH} \end{array}$

This compound is formed by heating monochloroacetic acid with solid toluidine. At ordinary temperatures, the two bodies simply unite to form a salt, but when 1 mol. chloroacetic acid and 2 mols. toluidine are heated together on the water bath, a reaction takes place, attended with a rise of temperature to 130° , and formation of a large quantity of hydrochloric acid:



To separate the tollyglycocine, the liquid is rendered slightly alkaline with ammonia; the toluidine thereby separated is removed by agitation with ether; the aqueous solution is evaporated to dryness on the water-bath to remove excess of ammonia; the residue redissolved in water; and the greater part of the hydrochloric acid removed by means of recently precipitated silver oxide. The solution is then again made alkaline with ammonia; the dissolved chloride, together with a small quantity of oxide of silver, is decomposed by hydrogen sulphide; the filtrate repeatedly evaporated to dryness and redissolved in water; and the solution, after renewed addition of silver oxide, again treated in the same manner. The rather dark-coloured liquid thus obtained, which no longer contains a trace of chlorine, is then boiled with charcoal and evaporated to dryness; and the residue, after washing with ether, is several times alternately dissolved in alcohol and in water. On evaporating the water or alcohol from these solutions, the tollylamidoglycollic acid remains as a viscid oil which solidifies in beautiful microscopic needles; and by slow evaporation of the alcoholic solution it may be obtained in larger crystals having a yellowish tinge. It is nearly insoluble in ether, melts at about 145° , and decomposes at about 170° . Its solutions have an acid reaction; the silver salt blackens quickly on exposure to the air, and almost instantly when heated; the lead salt appears to be more stable.

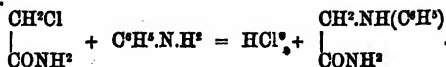
Tollylamidoglycollic acid has not yet been obtained quite pure, but its mode of formation and that of its derivatives, and the properties of these bodies, leave no doubt as to its composition: it might perhaps be obtained pure by decomposition of the lead salt (P. J. Meyer, *Deut. Chem. Ges. Ber.* viii. 1158).

Ethyl Tollylamidoglycollate, $\text{CH}_2\text{NH}(\text{C}^6\text{H}_7) - \text{COOC}^2\text{H}_5$, is prepared like the corresponding phenyl-compound (p. 880) by heating 1 mol. ethyl monochloroacetate with 2 mols. toluidine over an open fire, till the mass, after a somewhat violent reaction, suddenly solidifies to a crystalline pulp. The product, which no longer smells of chloroacetic ether, is then removed from the fire and dissolved in alcohol, and the solution is mixed with water, which throws down an oil solidifying at ordinary temperatures. After repeated solution in alcohol, and careful treatment of the cooled solution with water, the tollylamidoglycollic ether is obtained in white nacreous laminae which melt at 48° – 49° , dissolve but sparingly even in hot water, with moderate facility in cold alcohol, very easily in hot alcohol and in ether, also in hydrochloric ether. Hence it is advisable in preparing this body—as in the case of the corresponding phenyl-compound—to use a slight excess of chloroacetic ether (Meyer, *ibid.* 1159).

Glycollamides (P. J. Meyer, *Deut. Chem. Ges. Ber.* viii. 1154–1164).

1. Phenylamidoglycollamide, $\text{C}^6\text{H}^{10}\text{N}_2\text{O} = \begin{array}{c} \text{CH}_2\text{NH}(\text{C}^6\text{H}_5) \\ | \\ \text{CONH}^2 \end{array}$. *Phenylglycocinamide*.

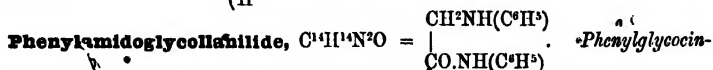
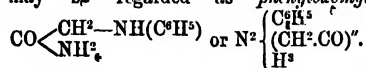
Phenyl-oxyethylene carbamide.—This compound is formed by the action of aniline on chloracetamide:



When 1 mol. chloracetamide is cautiously heated with 1 mol. aniline till the whole is fused, and the temperature is kept at the same degree till the liquid exhibits a strong reaction of hydrochloric acid, a product is obtained which dissolves in hot water, and separates on cooling as a white crystalline body purifiable by recrystallisation. This substance is phenylamidoglycollamide. It crystallises in microscopic

needles, melts at 133°, dissolves very easily in ether, alcohol and hot water, and with moderate facility in cold water.

If the group or radicle CH^2-CO or $\text{C}^2\text{H}^2\text{O}$ be called *oxethylene*, this compound may be regarded as *phenyloxethylene-carbamide* or *phenyloxethylene-urea*

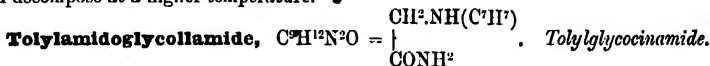


anilide.—When chloracetanilide is boiled with a slight excess of aniline till the whole is dissolved, the excess of aniline then removed by hydrochloric acid, and the residual oil boiled with a large quantity of water, phenylamidoglycollanilide is obtained as a body melting at 110°–111°, slightly soluble in cold, more freely in hot water, also in alcohol and in ether, and forming a well-crystallised hydrochloride (Meyer). Wilm a. Wischin obtained the same compound by the action of aniline on phenylamidoglycollic acid (phenyl-glycocine) and its ethers; also by that of aniline hydrochloride on phenyl-glycollamide, and directly by boiling chloracetyl chloride with excess of aniline.



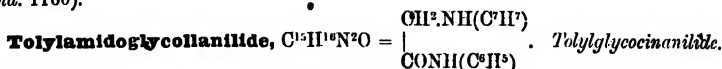
is digested for several hours in a sealed tube with moderately concentrated alcoholic ammonia, the product evaporated till it no longer smells of ammonia, and the resulting liquid mixed with water, a white crystalline precipitate is obtained, which dissolves in hot water, and separates from the solution in dazzling white needles often several inches long, having the composition of phenylamidodiglycollamide.

This compound melts at 140.5°, dissolves easily in ether and in alcohol, with moderate facility in hot water, sparingly in cold water. When boiled with soda-ley it gives off aniline. Its *hydrochloride* crystallises from hot hydrochloric acid in silvery needles and laminae; the *nitrate* in splendid white needles which melt at 172° and decompose at a higher temperature. •



Tolyl-oxethylene-carbamide.—Prepared by heating 1 mol. chloracetamide with 1 mol. toluidine at the temperature of the water-bath till a clear liquid is obtained, leaving this liquid to cool, and repeating the operation. The product is dissolved in hydrochloric acid, from which it separates by rapid cooling in small shining laminae, by slow cooling in needles and prisms. If contaminated with undecomposed chloracetamide, it may be purified by recrystallisation from hot water. If more than 1 mol. of toluidine has been used, the product also contains tolyl-amidacetoluide and sal-ammoniac, which may also be removed by solution in a moderately large quantity of hot water.

Tolylamidoglycollamide melts at 162°–163°, turning brown at the same time. It is sparingly soluble in cold water, moderately in ether, very easily in hot water and alcohol. When heated above its boiling point it gives off toluidine (Meyer. *ibid.* 1160).



Prepared by heating 1 mol. chloracetanilide with rather more than 2 mols. toluidine over an open fire till large quantities of hydrochloric acid are given off, and pouring the product into water, whereby an oil is separated, which quickly solidifies after the excess of toluidine has been removed by hydrochloric acid. After several recrystallisations from hot water, the compound is obtained in slender white needles, insoluble in cold water, sparingly soluble in hot water, easily in alcohol and ether, melting at 82°–83°.



toluidide.—This compound may be obtained: 1. By fusing 1 mol. chloracetamide with 2 mols. toluidine, and recrystallising the product from alcohol. 2. By fusing chloracetyl chloride or chloracetoluide with excess of toluidine, and crystallising from alcohol after addition of hydrochloric acid. 3. It is best prepared by heating a mixture of 1 mol. monochloracetic acid and 3 mols. toluidine over an open fire till a

violent reaction sets in, indicated by the rapid formation of bubbles within the liquid. The vessel is then to be removed from the fire, the action allowed to go on quietly to the end, and the solidified mass boiled with water to remove toluidine hydrochloride. By repeatedly crystallising the residue from alcohol, till the mother-liquor appears quite colourless, the tolylamidoglycollotoluide is obtained in white silvery laminae very slightly soluble in hot water, rather sparingly in cold alcohol, easily in hot alcohol and in ether. It melts at 136° , and when heated above this temperature, turns dark brown and gives off toluidine. It is not altered by heating with water to 200° , but when boiled with baryta-water it gives off toluidine. The hydrochloride, formed by passing hydrochloric acid over the compound heated to 100° , is decomposed by boiling with water.

Tolylamido-diglycollamides, or Tolyloxethylene-biurets. 1. The *monotolyl-compound*, $C^{11}H^{15}N^3O^2 = N(C^7H^7) \begin{smallmatrix} CH^2-CO-NH^2 \\ CH^2-CO-NH^2 \end{smallmatrix}$ is produced by heating tolylamidoglycollamide for some time in an open vessel. Toluidine is then given off, and on cooling, a crystalline residue is obtained which is somewhat difficult to dissolve in alcohol, whereas tolylamidoglycollamido is easily soluble therein. On washing this residue with alcohol to remove the unaltered amide, and repeatedly crystallising it from hot alcohol, the monotolyl-oxethylene-biuret is obtained in beautiful iridescent laminae and short thick prisms.

This compound may, however, be more easily prepared by heating monochloracetamide with an equivalent quantity of toluidine. It is also one of the bodies formed, as above mentioned, as secondary products in the preparation of tolylamidoglycollamido, in greater or smaller quantity, according as the mixture of 1 mol. chloracetamide and 1 mol. toluidine is kept in the state of fusion on the water-bath for a shorter or longer time. In this case, therefore, the biuret is formed at a temperature much below the melting point of the tolylamidoglycollamide, perhaps in consequence of the presence of free hydrochloric acid which abstracts toluidine. On treating the product with a small quantity of cold alcohol, the tolyloxethylene-biuret remains as a sparingly soluble body, which, when recrystallised from hot alcohol, likewise separates in iridescent laminae and prisms. It melts without decomposition at 250° , dissolves very sparingly in water, slightly in cold, more easily in hot alcohol and ether.

By due attention to the course of the reaction, it is possible to prevent the formation either of this body or of the tolylamido-glycollamide. If the former is produced, it is almost always accompanied by a third body, which may be separated from the biuret by treating the mass with a small quantity of alcohol, filtering, and mixing the filtrate with water; this third body then separates in very slender needles, and may be purified by redissolution in alcohol and precipitation with water. If all the three bodies are formed at once, the amide is first removed by treatment with a small quantity of boiling water, and the residue is treated as above.

This third body is the nitril of tolyl-glycoccine, or tolylamidacetonitril, $CH^2.NH(C^7H^7)-CN$, and is formed by abstraction of water from tolylamidoglycollamido, $CH^2.NH(C^7H^7)-CONH^2$ in the same way as acetonitril from acetamide (Meyer, *Deut. Chem. Ges. Ber.* viii. 1163).

Ditolylamido-diglycollamide, or Ditolyl-oxethylene-biuret, $NH \begin{smallmatrix} CH^2-CO-NH(C^7H^7) \\ CH^2-CO-NH(C^7H^7) \end{smallmatrix}$ (*Diglycollamidsäureditoluidid*). This compound is prepared, like the corresponding phenyl-compound, by heating chloracetoluide with moderately concentrated alcoholic ammonia in sealed tubes to 100° for several hours, concentrating the product, and precipitating with water. A crystalline precipitate is thereby obtained, which may be purified by repeated solution in alcohol, precipitation with water, and final recrystallisation from very dilute alcohol.

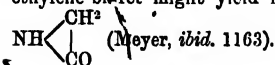
Tolylamido-diglycollamide crystallises in rosettes of long soft silky needles, melts at 149.5° , dissolves easily in ether and hot alcohol, with moderate facility in cold alcohol, sparingly in water even at the boiling heat. With acids and bases it behaves like the analogous phenyl-compound (Meyer, *ibid.* 1155).

Tritolylamido-diglycollamide, or Tritolyl-oxethylene-biuret, $C^{23}H^{27}N^3O^2 = N(C^7H^7) \begin{smallmatrix} CH^2-CO-NH(C^7H^7) \\ CH^2-CO-NH(C^7H^7) \end{smallmatrix}$ (*Diglycollamidsäuretritolidid*), is formed by heating tolylamidoglycollotoluide in an open vessel to about 160° – 170° . Large quantities of toluidine are then given off, and the product on cooling solidifies to well-defined needles. In sealed tubes the reaction does not take place below 235° . The product is repeatedly crystallised from alcohol—in the latter case with addition of hydrochloric acid—and finally separates in very beautiful long

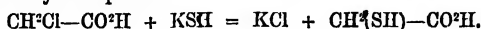
white needles, which melt at 251° . It is nearly insoluble in water, slightly soluble in cold alcohol and ether, freely soluble in the same liquids at higher temperatures.

By further heating of the oxethyleno-biurets formed as above, it might be possible—by elimination of a second molecule of an amino—to obtain a homologue of isocyanic acid or carbimide, CONH^{\cdot} . One of these homologues, producible from tritolyloxethyletho-biuret, would have the composition $\text{N}(\text{C}^{\cdot}\text{H}^{\cdot})\begin{matrix} \text{CH}^2 \\ \diagup \\ \text{CO} \end{matrix}$, and monotoxylox-

ethylene-biuret might yield in like manner the next homologue of carbimide, viz.



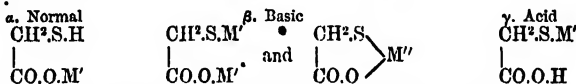
Thioglycollic acid, $\text{C}^{\cdot}\text{H}^{\cdot}\text{O}^{\cdot}\text{S} = \text{HS}-\text{CH}^2-\text{COOH}$ (Claesson, *Nebe's Annalen*, clxxxvii. 113). This acid is formed, together with thiodiglycollic acid, $\text{C}^{\cdot}\text{H}^{\cdot}\text{SO}^{\cdot} = \text{COOH}-\text{CH}^2-\text{S}-\text{CH}^2-\text{COOH}$ (v. 776), by the action of monochloroacetic acid on potassium hydrosulphide:



To prepare it, crystallised chloroacetic acid (1 mol.) is added to a concentrated solution of potassium hydrosulphide (2 mols.); the product, at the end of the reaction, is concentrated on a water-bath, and filtered; the filtrate is treated with excess of absolute alcohol; the filtered alcoholic solution is evaporated; the residual salt dissolved in water and decomposed by sulphuric acid; the thioglycollic acid thereby separated is extracted by ether; and the ether evaporated.

Thioglycollic acid thus obtained is a colourless uncrystallisable oil, soluble in all proportions in water, alcohol, and ether. It has a faint odour, which becomes suffocating when the acid is warmed. It appears to be capable of volatilising without decomposition when slowly heated, but decomposes when quickly heated, giving off a very unpleasant odour.

Thioglycollic acid forms three classes of salts, represented by the following formulæ:



a. Thioglycollic acid is a strong acid, and forms salts of this type with the alkalis, alkaline earths, and some of the metals of the iron group, generally with those metals which have a greater affinity for oxygen than for sulphur. They are obtained by dissolving the oxides or carbonates in the acid. They are very soluble, and for the most part do not crystallise well.

The normal potassium salt, $\text{HS.CH}^2\text{CO.OK}$, is very soluble in water and crystallises therefrom in spherical groups of small needles containing 1 mol. H^2O . It dissolves very readily in alcohol, but the solution gradually absorbs water, and the salt is then for the most part deposited in the anhydrous state. It is not deliquescent. The anhydrous salt dissolves in small quantity in boiling alcohol, and crystallises on cooling in capillary needles. It oxidises in contact with the air. On treating it with excess of potassium carbonate, carbon dioxide is given off, and the dipotassic salt $\text{KS.CH}^2\text{CO.OK}$ is produced.

Barium salt, $(\text{HS.CH}^2\text{CO.O})^2\text{Ba}$.—This salt rises up on spontaneous evaporation to a gummy mass. It is insoluble in alcohol, and is precipitated thereby from its aqueous solution in the amorphous state.

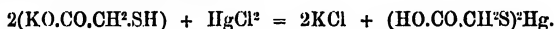
The ethylic ether, $\text{HS.CH}^2\text{CO.OCC}^2\text{H}^5$, is easily obtained by boiling the acid with absolute alcohol, and adding a few drops of strong hydrochloric acid. It is a colourless, very fetid oil, heavier than water and somewhat soluble therein. It begins to boil at about 165° , but the boiling point slowly rises to 250° , and the ether partly decomposes, giving off hydrogen sulphide and forming ethylic thiodiglycollate, which passes over with the undecomposed portion. If the boiling be somewhat prolonged, this decomposition is nearly complete. The two ethers may be easily distinguished by the fact that the thiodiglycollic ether, when treated with alcoholic potash, immediately forms a crystallisable potassium salt, which is not the case with the thioglycollic ether.

b. The basic thioglycollates containing univalent metals are distinguished from the acid salts (p. 886) by the circumstance that the atom of metal which is attached to the sulphur may be removed by the weakest acids, whereas in the metallothioglycollic acids this removal can be effected only by hydrogen sulphide. The only basic thioglycollates known are those of the alkalis and alkaline earths. The former are uncrystallisable and difficult to obtain pure.

The barium salt, $\left. \begin{array}{l} \text{CH}_2\text{S} \\ | \\ \text{CO.O} \end{array} \right\} \text{Ba} + 3\text{H}_2\text{O}$, may be prepared by mixing the normal potassium salt with ammonia and barium chloride; by mixing the potassium salt or the free acid with barium hydrate; or by mixing the normal barium salt with ammonia. It is crystalline, nearly insoluble in cold water, and is but slowly dissolved by warm water. Carbonic acid decomposes it readily into carbonate and normal thioglycollate of barium.

7. Metallo-thioglycollic acids, $\left. \begin{array}{l} \text{CH}_2\text{S.M'} \\ | \\ \text{CO.OH} \end{array} \right\}$. Thioglycollates having the metal in immediate connection with the sulphur are formed only by those metals which have a great affinity for sulphur. Each of these compounds is a true acid capable of forming salts with other metals. On account of their tendency to pass into compounds in which the hydroxylic hydrogen is also replaced by a metal, only the three following have been obtained in a state somewhat approaching to purity.

Mercuriothioglycollic acid, $\text{C}^4\text{H}^4\text{O}^2\text{S}^2\text{Hg} = \text{CO}^2\text{H}.\text{CH}^2\text{S}.\text{Hg}.\text{CH}^2\text{S}.\text{CO}^2\text{H}$, is prepared either by mixing free thioglycollic acid with mercuric oxide, whereupon a brisk reaction takes place,—or, better, by mixing a cold solution of the potassium salt with mercuric chloride, the mercuriothioglycollic acid then immediately separating as a felted mass of long slender needles:



Mercuriothioglycollic acid is nearly insoluble in cold water, but dissolves easily in boiling water and in alcohol, and crystallises in long slender needles resembling cotton-wool when dry, or in short flat prisms. It has an acid reaction, and unites with nearly all metals except the alkali-metals, forming sparingly soluble and for the most part crystallised salts. It decomposes metallic salts, taking the metal to itself, and forming acid salts with barium, aluminium, and manganese, neutral salts with lead, mercury, and silver. These salts decompose only at very high temperatures, leaving pure or nearly pure metallic oxides.

The barium salt, $\text{BaH}^2(\text{O.CO.CH}_2\text{S})^2\text{Hg}^2$, formed on mixing hot solutions of the acid and barium chloride, separates in ramified groups of microscopic crystals. The aluminium salt, $\text{Al}^3\text{H}^3(\text{O.CO.CH}_2\text{S})^3\text{Hg}^3$, formed from alum and the free acid, resembles the barium salt. The manganese salt, $\text{MnH}^2(\text{O.CO.CH}_2\text{S})^2\text{Hg}^2$, resembles the two preceding in its mode of formation and its external characters. The lead salt, $\text{Pb}(\text{O.CO.CH}_2\text{S})^2\text{Hg}$, is formed as an amorphous precipitate, on mixing a solution of the acid with lead acetate. The mercuric salt, $\text{Hg}(\text{O.CO.CH}_2\text{S})^2\text{Hg}$, is produced in like manner from mercuric chloride and the free acid; also on adding mercuric chloride to potassium thioglycollate. It is amorphous or indistinctly crystalline. The silver salt, $\text{Ag}^2(\text{O.CO.CH}_2\text{S})^2\text{Hg}$, is a white amorphous precipitate formed from the free acid and silver nitrate. Its analysis gave 33.49 per cent. silver instead of the calculated quantity 36.18, showing that the hydrogen in the acid had not been completely replaced by silver.

Cuprosothioglycollic acid, $(\text{HO.CO.CH}_2\text{S})^2\text{Cu}^2$.—Potassium thioglycollate gives with cupric salts a bluish-black precipitate, which, on further addition of potassium salt, becomes nearly white, in consequence of the reduction of the cupric salt formed in the first instance to a cuprous salt. In this respect the behaviour of thioglycollic acid to cupric salts is similar to that of xanthic acid and analogous compounds, and of mercaptan. The white compound has the composition above given, and reacts altogether like a cuprous compound, dissolving readily in potassium cyanide and sodium thiosulphate, and without colour in ammonia. In the moist state it blackens, being resolved into the cuprous salt, $\text{Cu}^2(\text{O.CO.CH}_2\text{S})^2\text{Cu}^2$, and free thioglycollic acid, but this change may be prevented by addition of acetic acid. The compound dissolves readily in hydrochloric acid and in alkalis, forming salts. By addition of other metallic salts to the alkaline solution, amorphous precipitates are produced, and the metallic hydroxide formed at the same time may be extracted by acetic acid. The barium salt, $\text{Ba}(\text{O.CO.CH}_2\text{S})^2\text{Cu}^2$, is a greyish amorphous precipitate.

Bismuthothioglycollic acid, $(\text{HO.CO.CH}_2\text{S})^3\text{Bi}$, is formed, on mixing potassium thioglycollate with a solution of bismuth nitrate, as a yellow precipitate which redissolves on agitation, but becomes constant on further addition of the bismuth salt. This precipitate is a white soft mass which soon becomes hard and brittle; it melts at 30° – 35° . On continued addition of bismuth nitrate it yields amorphous yellow precipitates which do not melt, and the easily fusible compound itself, when heated on the water-bath, loses weight and becomes infusible.

Argento-, Plumbo-, and Cadmiouthioglycollic acids.—These acids have

not been obtained in a state even approaching to purity, the precipitates which are formed by metallic salts in a solution of potassium thioglycollate, consisting of salts of these acids containing the same metal that enters into the acid itself (p. 884).

Argentothioglycollate of Silver, $\text{Ag} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S} \cdot \text{Ag}$, is formed on adding silver nitrate to free thioglycollic acid or the potassium salt, as a white, perfectly amorphous mass, which is not altered by light; is quite insoluble in acetic and in cold nitric acid; shrinks up on drying to a hard dark-coloured mass; and requires a somewhat high temperature to decompose it.

Cadmiothioglycollate of Cadmium, $\text{Cd}(\text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S})_2 \cdot \text{Cd}$, is obtained as an amorphous or indistinctly crystalline mass on adding potassium thioglycollate to a solution of cadmium sulphate, the latter being kept in excess. It dissolves readily in the potassium salt and in hydrochloric acid.

Plumbothioglycollate of Lead, $\text{Pb}(\text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{S})_2 \cdot \text{Pb}$, obtained like the silver compound, is a white or slightly yellowish precipitate, amorphous at first, but crystallising after some time in distinct flat prisms. It is quite insoluble in acetic acid, but is dissolved by a large excess of nitric acid. If the potassium thioglycollate is added in excess, the precipitate is yellow and contains a much smaller proportion of lead.

Platinic chloride does not form a precipitate with thioglycollic acid, probably because the resulting platinothioglycollic acid is soluble in hydrochloric acid.

Thioglycollic Ethers, $\text{RS} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{OM}$ (R denoting an alcohol-radicle and M a metal or hydrogen); also called *Sulphacetic Ethers*. These compounds, first prepared by Blomstrand (*Deut. Chem. Ges. Ber.* iv. 717), have been further examined by Claesson (*ibid.* viii. 120).

Ethyl-thioglycollic acid, $\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COOH}$.—The ethylic ether of this acid is formed, with great rise of temperature, on mixing the alcoholic solutions of ethylic monochloracetate and sodium mercaptide, and, after filtration from the separated sodium chloride, may be precipitated by water. By heating the ether with baryta-water in sealed tubes, and decomposing the resulting barium salt with sulphuric acid, the ethyl-thioglycollic acid is obtained as an uncrystallisable oil. It is easily soluble in alcohol and ether, moderately soluble in water. It does not volatilise without decomposition, but may be distilled with vapour of water. Its salts dissolve readily in water and in alcohol; they do not bear so high a temperature as the phenyl-thioglycollates (p. 887). They are oxidised by nitric acid, and form a viscid brown precipitate with iron salts. The *potassium salt*, $\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COOK}$, forms deliquescent crystalline crusts, slightly soluble in alcohol. The *silver salt*, $\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COOAg} + \text{H}_2\text{O}$, is a crystalline precipitate which does not give off its water over sulphuric acid. The *barium salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Ba}$, and the *calcium salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Ca}$, crystallise in radiate groups of needles. The *lead salt* is a viscid mass; the *magnesium salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Mg} + 3\text{H}_2\text{O}$, and the *zinc salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Zn} + 2\text{H}_2\text{O}$, are crystalline masses. The *cadmium salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Cd} + \text{H}_2\text{O}$, forms prisms which melt and give off their water at 100° ; it is less soluble than the preceding salts. The *manganese salt* is of similar character. The *cobalt salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Co} + 2\text{H}_2\text{O}$, forms small violet-red very soluble prisms; the *nickel salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Ni} + 2\text{H}_2\text{O}$, is greenish, but in other respects like the cobalt salt. The *copper salt*, $(\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO})_2\text{Cu} + 2\text{H}_2\text{O}$, forms small shining rhombic plates which melt at 90° , and decompose with great facility.

The *ethylic ether*, $\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{C}^2\text{H}_5$, prepared as above described, is a strongly refractive oil, which has a strong odour, a density of 1.0469 at 4° , and melts at 187° – 189° .* It is not attacked by iodine, but bromine acts upon it strongly. Ammonia converts it into ethyl-thioglycollamide, $\text{C}^2\text{H}_5 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in long thin prisms, melts at 44° , dissolves easily in water and in alcohol, and cannot be volatilised without decomposition.

Ethylic Diethylsulphinodacetate, $\text{C}^2\text{H}_5 \cdot \text{S} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{I} \quad \text{COOC}^2\text{H}_5 \end{array}$, is formed by heating ethylic

ethylthioglycollate and methyl iodide in equal numbers of mols. to 120° in a sealed tube, and separates, on leaving the product to evaporate in a vacuum, in yellowish crystals. When agitated with silver oxide it yields a strongly alkaline solution.

Amylthioglycollic acid is a viscid liquid. Its ethylic ether boils at 230° , and has a density of 0.9797 at 4° . Its salts, except those of the alkali-metals, are but slightly soluble. The *zinc* and *cadmium salts* are white precipitates; the *copper salt* crystallises in slender needles; the *lead salt* is very easily fusible.

* Erlenmeyer & Lisenko (*Zetschr. Chem. Pharm.* 1862, 184) describe this ether as a liquid boiling at about 100° . The cause of this discrepancy appears to be that they prepared it with sodium mercaptide which had been somewhat altered by heat, as indeed appears from the fact that they were obliged to heat it with the chloroacetic ether in sealed tubes, whereas with unaltered sodium mercaptide a strong reaction takes place at ordinary temperatures.

Phenyl-thioglycollic acid, $C^6H^5.S.CH^2.COOH$.—The ethylic ether of this acid, prepared by the action of sodium phenyl-mercaptide on ethylic chloracetate in alcoholic solution, is decomposed by alcoholic potash like the corresponding ethyl-compound, yielding potassium phenyl-thioglycollate, which separates in crystalline spangles; and by decomposing this salt with hydrochloric acid, the free acid is obtained in the form of an oil which soon becomes crystalline. From a hot dilute solution it separates on cooling in thin brittle plates. It melts at 43.5° , and resolidifies at 28° . It dissolves in all proportions in alcohol and ether, slightly in cold, more readily in warm water, forming strongly acid solutions. It cannot be volatilised alone, but distils even with vapour of water. It is not decomposed by boiling with dilute acids. Its salts are, for the most part, slightly soluble in water, insoluble in alcohol; they may all, except the copper salt, be heated to 100° without alteration, but begin to blacken and decompose at 200° .

The potassium salt, $C^6H^5.S.CH^2.CO.OK$, crystallises in thin silky needles, moderately soluble in hot water; it is not decomposed either by boiling its solution or by fusing it with potash. The sodium salt, $C^6H^5.S.CH^2.CO.ONa$, may be produced directly by decomposing sodium monochloracetate with an alcoholic solution of sodium phenyl-mercaptide; it forms crusts composed of nodules. The ammonium salt forms crystalline crusts which melt with decomposition above 100° . The silver salt, $C^6H^5.S.CH^2.COOAg + H^2O$, is a white precipitate.

The following are represented by the general formula $(C^6H^5.S.CH^2.COO)^nM^n$.

Barium salt.—Anhydrous crystalline mass composed of slender needles; moderately soluble in hot water. **Calcium salt**. Anhydrous; groups of oblique tablets. **Lead salt**. Anhydrous; amorphous precipitate which soon hardens, and melts at 60° . **Magnesium salt**, $+ 3H^2O$. Shining scales containing $3H^2O$. **Zinc salt**, $+ 2H^2O$. Radiate groups of long needles having a silky lustre. **Cadmium salt**, $+ H^2O$. Shining scales. **Manganese salt**, $+ 5H^2O$. Bulky mass composed of oblique plates. **Cupric salt**. Anhydrous; amorphous precipitate of fine green colour. Easily alterable; becomes viscid when exposed in the moist state to the air; heated with water it yields tarry masses consisting of a basic salt. The normal salt dissolves easily in ammonia, and the solution when evaporated in a vacuum leaves blue prisms.

The cobalt, nickel, aluminium, ferric, and chromic salts are amorphous precipitates.

The ethylic ether, $C^6H^5.S.CH^2.CO.OCH^3$, is a liquid which in the pure state has a sweetish, aromatic, and not unpleasant odour, a specific gravity of 1.136 at 4° , and 1.1269 at 15° , and boils with partial decomposition at 276° – 278° . The amide, $C^6H^5.S.CH^2.CONH^2$, prepared from it crystallises from alcohol in small plates melting at 104° , easily soluble in alcohol, less soluble in water, very slightly soluble in ether.

Bromophenyl-thioglycollic acid, $C^6H^5.Br.S.CH^2.COOH$.—The ethylic ether of this acid is formed, with brisk reaction, on adding bromine to a solution of ethylic phenyl-thioglycollate in carbon disulphide. Treated with alcoholic potash, it yields the corresponding potassium salt, and this, when decomposed by hydrochloric acid, yields the free acid in shining slightly soluble needles melting at 112° .

Oxidation-products of Ethyl- and Phenyl-thioglycollic acid (Claesson, *loc. cit.*) By subjecting a salt of either of these acids to the action of a solution of potassium permanganate (not of nitric acid, or of chromic acid mixture), the sulphur contained in it may be oxidised, without further decomposition of the molecule, to SO^2 or SO^3 . In this manner the following acids have been obtained:—

Ethyl-sulphoglycollic acid, $C^2H^5.SO^2.CH^2.COOH$.—This acid, separated from its zinc salt by hydrogen sulphide, forms a thick uncrystallisable liquid, which dissolves very easily in water, as also do most of its salts. The potassium salt, $C^2H^5.SO^2.CH^2.CO^K$, crystallises from alcohol in small, colourless, very hygroscopic plates. The barium salt, $(C^2H^5.SO^2.CH^2.CO)^2Ba$, forms small nodules; the copper salt, $(C^2H^5.SO^2.CH^2.CO)^2Cu + 2H^2O$, rather large bluish plates, becoming anhydrous at 240° . The zinc salt and the silver salt are moderately soluble; the latter forms small needles. The lead salt forms small, very soluble plates.

Phenyl-sulphoglycollic acid, $C^6H^5.SO^2.CH^2.COOH$, is separated by hydrochloric acid from the concentrated solution of its potassium salt, as an oil; it dissolves in ether and is left on evaporation in the form of an oil which soon solidifies. By crystallisation from water, it is obtained in small monoclinic crystals which melt at 109° , have a very sour taste, and dissolve easily in alcohol and in ether. Its salts are more soluble than those of phenyl-thioglycollic acid, the potassium and zinc salts being even deliquescent. The silver salt, $C^6H^5.SO^2.CH^2.COOAg$, crystallises from boiling water in slender needles. The copper salt, $(C^6H^5.SO^2.CH^2.COO)^2Cu + 2H^2O$, forms small green moderately soluble tablets.

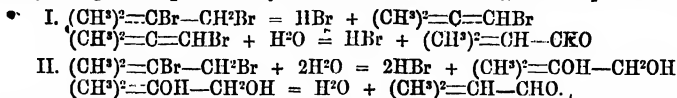
Phenyl-sulphiglycollic acid, $C^6H^5.SO.CH^2.COOH$, is produced when a salt of phenyl-thioglycollic acid is treated with half the quantity of permanganate required

to convert it into the sulpho-acid. It forms colourless crystals melting at 74° . The copper salt is a greenish amorphous precipitate.

GLYCOLS. *Action of Water.*—Carius found that ethylene bromide heated with water in a sealed tube to 150° – 180° , is resolved into acetaldehyde and hydrogen bromide (1st Suppl. 602):



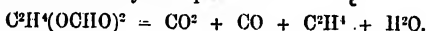
This conversion of a glycollic ether into an aldehyde might be supposed to take place either through the medium of the brominated hydrocarbon or through that of the corresponding glycol. Thus the conversion of isobutylene bromide into isobutyric aldehyde might be represented by either of the two following sets of equations:



Experiment shows, however, that bromisobutylene, $(\text{CH}^3)^2\text{C}=\text{CHBr}$, is not acted upon by water at 150° – 200° , whereas isobutylene glycol, $(\text{CH}^3)^2\text{COH}-\text{CH}^2\text{OH}$, heated with water in sealed tubes to 180° – 200° , is transformed, by elimination of H_2O into the corresponding aldehyde. The reaction must therefore be represented by the second pair of equations above given (Névolé, *Compt. rend.* lxxxiii. 228).

Action of Oxalic acid on Ethylene-glycol.—The reaction begins at 80° with evolution of pure carbon dioxide, while formic acid distils over, the distillate containing successively from 6.7 to 56.7 per cent. of that acid. The portions which distil over between 172° and 175° consist of pure ethylene diformate, $\text{C}^2\text{H}^4(\text{OCHO})^2$, and those obtained between 120° and 172° perhaps contain ethylene monoformate. The same bodies are produced, together with glycol and small quantities of free formic acid and methyl formate, by the action of potassium formate at 85° on a mixture of ethylene bromide and ethyl alcohol (Lorin, *Compt. rend.* lxxix. 367; *Bull. Soc. Chim.* [2], xxi. 409; xxii. 104).

Glycolic Diformin or Ethylene Diformate is also produced by heating ethylene glycol for some time to boiling in a reflux apparatus with 3 to 4 parts of 75–80 per cent. formic acid. On distilling the product, a mixture of the mono- and di-formins passes over between 170° and 180° ; and the diformin may be easily isolated by again treating the mixture with about 1 part of crystallisable formic acid and rectifying the product. Glycolic diformin is a colourless, very mobile liquid having a peculiar odour and boiling without decomposition at 174° . When heated in sealed tubes it is decomposed in the manner shown by the equation



At the same time the water thus produced saponifies a portion of the formin, so that the residue contains small quantities of glycol and formic acid (Henninger, *Bull. Soc. Chim.* [2], xxi. 242).

On Glycolic Ethers, see ETHYLENE COMPOUNDS, pp. 752–755.

Glycolic Chlorosulphonic acid or *Ethylene-chlorosulphonic acid*, $\text{C}^2\text{H}^4\text{Cl}(\text{SO}^3\text{H})$, is formed, together with chloral, by the action of sulphuric acid on the compound $\text{CCl}^2-\text{CH}\begin{smallmatrix} \text{O}-\text{CH}^2-\text{CH}^2\text{Cl} \\ \text{OH} \end{smallmatrix}$, produced by the union of glycolic monochlorhydrin with chloral (L. Henry).

GLYCOLYL-TRICARBAMIDE, $\text{CS}\begin{smallmatrix} \text{NH}\cdot\text{CH}^2 \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$. See CARBAMIDES (TRIO-), p. 400.

GLYCOPROTEIN. See PROTEIDS.

GLYCOSAMINE, $\text{C}^6\text{H}^{13}\text{NO}^3 = \text{COH}(\text{CHOH})^4\cdot\text{CH}^2\cdot\text{NH}^2$ (G. Ledderhose, *Deut. Chem. Ges. Ber.* ix. 1260). The hydrochloride of this base, $\text{C}^6\text{H}^{13}\text{NO}^3\cdot\text{HCl}$, is formed by boiling chitin for half-an-hour with strong hydrochloric acid. The chitin then dissolves, forming a blackish-brown solution, which when evaporated leaves the hydrochloride in the form of shining crystals mixed with a black amorphous mass. If chitin be similarly treated, with addition of metallic tin, the solution formed has only a slight yellowish-brown colour, and the formation of the amorphous substance is entirely avoided. The crystals amount to about 40 per cent. of the chitin employed. They have a decidedly sweet taste, dissolve freely in water, sparingly in alcohol, forming acid solutions. They give with soda ley and copper sulphate a dark-blue solution, which deposits cuprous oxide on warming.

Glycosamine hydrochloride is dextrogyrate, having a specific rotatory power, $[\alpha]_D =$

70·6. It appears to ferment with yeast. The solution of the free base has an alkaline reaction, and decomposes with brown coloration when evaporated.

The constitution of glycosamine is that of a carbohydrate in which HO is replaced by NH².

GLYCYRRHIZIN and **GLYCYRRETIN**. Z. Roussin (*Arch. Pharm.* [3], viii. 156) observes that glycyrrhizin is a tasteless substance, and ascribes the sweet taste of liquorice-root to an ammonia-compound of glycyrrhizin, which, like the compounds formed by that substance with potash and soda, has a very sweet taste. According to Habermann (*Deut. Chem. Ges. Ber.* x. 870), amorphous commercial glycyrrhizin yields to glacial acetic acid a body which crystallises from alcohol in hemispherical groups of needles. It dissolves readily in water and in aqueous alcohol, less freely in absolute alcohol, scarcely at all in ether. In its reactions it resembles the amorphous compound described by Gorup-Besanez (ii. 920), but has a different composition, and when boiled with dilute sulphuric acid yields a resinous body having the sweet and acrid taste of the original substance.

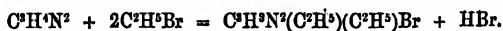
Griessmeyer finds that glycyrrhizin is resolved into glycyrretin and fermentable sugar by boiling, not only with dilute acids, but also with saline solutions, and even with water (*Dingl. pol. J.* ccix. 228).

According to Wosolsky a. Benedikt (*Deut. Chem. Ges. Ber.* x. 1158), glycyrretin fused with potassium hydroxide yields nothing but paraoxybenzoic acid.

GLYOXAL, C²H²O² = HOC—COH. Debus obtained this compound, together with glyoxalic acid and other products, by the action of nitric acid on alcohol (ii. 920). According to Lubawin (*Deut. Chem. Ges. Ber.* viii. 768), it is better to use a 50 per cent. aqueous solution of aldehyde. In cylinders holding a quarter of a litre, the oxidation is completed in a week; and the evaporated product consists mainly of glyoxal. 100 grams of aldehyde yield from 45 to 100 of the recrystallised compound of glyoxal and acid sodium sulphite. Lubawin has detected formic acid amongst the products of the action of ammonia on glyoxal, and explains the reaction in the same manner as Debus.

GLYOXALINE, C²H⁴N². This base, which Debus obtained, together with glycosine, C⁶H⁶N⁴, by the action of ammonia on glyoxal (ii. 921), has been further examined by G. Wyss (*Deut. Chem. Ges. Ber.* ix. 1543; x. 1365). To prepare it, the evaporated residue of glyoxal obtained by Lubawin's process is treated very gradually with ammonia in slight excess, the temperature being kept down. Glycosine then separates as a brown powder, and the filtered solution contains the glyoxaline together with ammonia, chiefly as acetate. This liquid is boiled with milk of lime to expel the ammonia, then evaporated to a syrup, treated with absolute alcohol to separate mineral salts, and filtered; the residue is strongly pressed to separate as much as possible of the liquid; and the whole of this liquid is distilled from a wide-necked retort. After one rectification the glyoxaline is perfectly pure, and solidifies to a radiate, dazzling-white crystalline mass. It dissolves easily in water, alcohol, and ether, but is not deliquescent, and crystallises in thick nacreous prisms. It has an alkaline reaction, and emits a slight fishy odour when warmed. Its vapour-density, determined in sulphur-vapour (it suffers scarcely any decomposition at 447°), is 2·35: hence its molecular formula is C²H⁴N² (not C⁴H⁸N⁴, as supposed by Lubawin).

Reactions.—1. Acetic anhydride and the chlorides of acetyl and benzoyl are without action on glyoxaline, even when heated with it, or, at least, form only addition-products. From this it might be inferred that glyoxaline is a tertiary base. But if it be boiled for some hours with ethyl bromide, the syrup remaining after evaporation on the water-bath taken up with water, the bromine removed by freshly precipitated silver chloride, and platonic chloride added to the concentrated solution, then gradually separates a salt having the composition [C²H³N²(C²H⁵)(C²H⁵)Cl]²PtCl⁴ + $\frac{1}{2}$ H²O. Hence the reaction between glyoxaline and ethyl bromide takes place as represented by the equation:



By treating the bromethylate with moist silver oxide, the hydroxide may be obtained as a strongly alkaline liquid, which, when dried in a vacuum over sulphuric acid, changes to a deliquescent crystalline solid. Benzyl chloride acts on glyoxaline in a perfectly similar way.

Glyoxaline is quite unaffected by chromic acid, and by reducing agents of all kinds, but potassium permanganate oxidises it completely, yielding formic acid and carbon dioxide.

When concentrated solutions of glyoxaline sulphate and potassium nitrite, or of

the hydrochloride and *silver nitrite*, are heated for a long time, the mixture evaporated, and the residue exhausted with absolute alcohol, a nitroso-derivative possessed of acid properties is obtained. The alkaline salts of this body are reddish-brown, and give with solutions of metallic salts, amorphous variously-coloured precipitates.

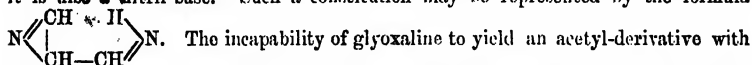
Tribromoglyoxalinic acid, $C^3HBr^3N^2$, is produced, together with glyoxaline hydrobromide, by the action of bromine on an ethereal or (better) aqueous solution of glyoxaline. In the latter way a bright brown precipitate is formed, which may be crystallised from a large quantity of boiling water. It is readily soluble in alcohol, almost insoluble in cold water, and sparingly soluble in ether, chloroform, and carbon disulphide; soluble in alkalis, and precipitated by acids. With the exception of hydrocyanic acid, it is the only known organic acid not containing oxygen. Most of its salts are insoluble. The silver-compound, when boiled with ethereal solutions of methyl or ethyl iodide, gives methyl- and ethyl-tribromoglyoxalates, well-crystallised bodies, insoluble in water and alkalis, soluble in alcohol and in ether. On treating them for some time in warm alcoholic solution with *sodium-amalgam*, the bromine contained in them is displaced by hydrogen, yielding methyl- and ethyl-glyoxaline, $C^3H^3(CH^3)N^2$ and $C^3H^3(C^2H^5)N^2$, which are oily bases forming deliquescent hydrochlorides and crystalline platinoclorides, that of the methyl-derivative crystallising in slender yellow needles, and that of the ethyl-derivative in yellowish prisms.

Silver-glyoxaline is obtained as a granular insoluble precipitate when silver nitrate is added to a solution of glyoxaline—

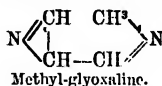
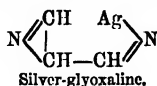
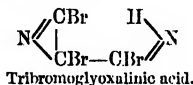
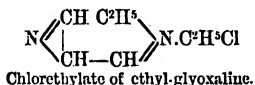


or better by adding caustic soda to a mixture of glyoxaline and silver nitrate. The reaction of acetyl chloride on this body gives unsatisfactory results; the iodides of methyl and ethyl, however, act upon it in the cold, giving, besides small quantities of the above-mentioned homologues, insoluble doughy compounds, not yet investigated.

Constitution of Glyoxaline.—The facility with which one of the atoms of this base can be replaced by metals and alcohol-radicles makes it probable that glyoxaline is an imide-base, and its reaction with the alcoholic iodides points to the conclusion that it is also a nitril-base. Such a constitution may be represented by the formula



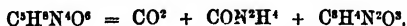
acetyl chloride is no proof of the absence of an imidogen-group, since the phenylated guanidines, as well as some other bases, exhibit the same peculiarity. Assuming this constitution, some of the above bodies may be thus formulated:



Glycosine, the base formed simultaneously with glyoxaline, has been but little studied. It forms, however, with silver nitrate, a double salt, $C^3H^4N^4.AgNO^3$, and exhibits the remarkable property of dissolving easily not only in acids but likewise in soda-ley at the boiling heat.

GLYOXYL-CARBAMIDE or **GLYOXYL-UREA**, $C^3H^4N^2O^3 = CH^3(C^2HO^2)N^2O$. (L. Medieus, *Liebig's Annalen*, clxxv. 230; *Deut. Chem. Ges. Ber.* ix. 1162; x. 544.) This appears to be the constitution of an acid, isomeric with lantanuric acid, the potassium salt of which was obtained by Strecker, with brisk evolution of carbon dioxide, on adding acetic acid to a solution of the potassium salt of the acid $C^3H^3N^2O^3$, called by Strecker *oxonic acid* (q.v.)

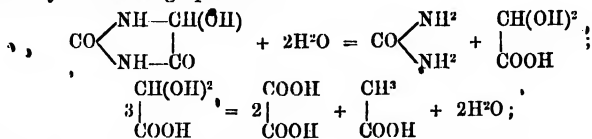
It is also formed, together with urea and carbon dioxide, by boiling uroxanic acid with water:



The resulting solution concentrated and left to evaporate leaves a syrupy liquid, and on neutralising this with barium carbonate, dissolving in water, and adding alcohol, a precipitate is obtained consisting of the *barium salt of glyoxyl-urea*, $(C^3N^2H^3O^3)^2Ba$.

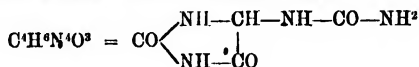
The *potassium salt* is a crystalline powder; the *silver salt* an amorphous powder. Glyoxyl-urea itself crystallises in thick shining needles, slightly soluble in cold, easily in hot water.

Glyoxyl-urea breaks up, under the action of potassium hydroxide, in the manner indicated by the following equations:—



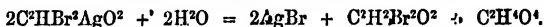
the ultimate products being ammonia, acetic acid, and oxalic acid.

GLYOXYL-DICARBAMIDE or -DIUREIDE,

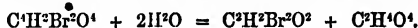


This is the constitution of allantoïn, which may in fact be formed by heating glyoxylic acid with urea (p. 57).

GLYOXYLIC ACID, $\text{C}^2\text{H}^2\text{O}^3$ (Debus); $\text{C}^2\text{H}^4\text{O}^4 = \text{CH}(\text{OH})^2-\text{CO.OH}$ (Perkin). See ii. 922 and 1st *Suppl.* 650. The constitution of this acid has been further examined by Perkin (*Chem. Soc. Jour.* 1877, ii. 88). The glyoxylic acid was prepared by decomposition of dibromacetic acid, which is readily obtained by treating acetic anhydride with bromine, and subjecting the resulting monobromacetic acid to the further action of bromine at the boiling heat and in sunshine. The silver salt of this acid, when boiled with water, is resolved, with rise of temperature and formation of silver bromide, into dibromacetic and glyoxylic acids:

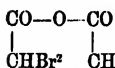


The same salt, boiled with alcohol, yields a mixture of (probably) ethylic dibromacetate and ethylic diethylglyoxylate, $\text{CH}(\text{OC}^2\text{H}^5)^2-\text{COOC}^2\text{H}^5$. Heated to 100° with dry ethyl oxide, silver dibromacetate yields an oily product which, when purified by agitation with ether and sodium carbonate, has the composition $\text{C}^4\text{H}^2\text{Br}^2\text{O}^4$, its formation being represented by the equation $2\text{C}^2\text{HBr}^2\text{AgO}^2 = 2\text{AgBr} + \text{C}^4\text{H}^2\text{Br}^2\text{O}^4$; and this oil, when treated with water, is decomposed into dibromacetic and glyoxylic acids:



It appears to possess the properties of an anhydride, and may be regarded either as a

dibromacetoglyoxyllide, $\text{O} \begin{array}{l} \text{CO} \\ | \\ \text{OH}(\text{OC}^2\text{HBr}^2\text{O}) \end{array}$, or as a double anhydride,

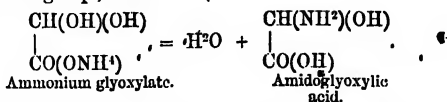


The aqueous solution of glyoxylic acid, if quickly evaporated over sulphuric acid in a vacuum, leaves merely a gummy mass; but by slower evaporation over sulphuric acid under the ordinary atmospheric pressure, the acid is obtained in crystals which are apparently oblique rhombic prisms, but it is not easy to make out their form, as they are small and rather confused; moreover, they are produced in a very thick liquid and deliquesce rapidly when taken out. The acid is very soluble in water and in alcohol, tastes very much like tartaric acid, melts to a syrupy liquid when heated, and cannot be distilled without decomposition.

When heated to $120^\circ-130^\circ$ for five hours with absolute alcohol, it yields a colourless liquid consisting of the ethylic ether of diethyl-glyoxylic acid, $\text{CH}(\text{OC}^2\text{H}^5)^2-\text{COOC}^2\text{H}^5$.

The *ammonium salt*, obtained by decomposing calcium glyoxylate with ammonium oxalate, or by neutralising glyoxylic acid with ammonia, has, after evaporation in a vacuum, the composition $\text{C}^2\text{H}^4\text{N}^2\text{O}^3$ or $\text{C}^2\text{H}(\text{NH}^4)\text{O}^3$, and is the compound which most favours the formula $\text{C}^2\text{H}^2\text{O}^3$ proposed for glyoxylic acid by Debus. This salt, however, though quite neutral to test-paper, when freshly prepared, like the glyoxylates of potassium and sodium, becomes acid when its solution is evaporated in a vacuum, even after having been rendered slightly alkaline with ammonia, which dissolves it with great facility. From these properties Perkin infers that the compound in question is not a true ammonium salt, but an *amido-acid* formed from the ammonium glyoxylate

(produced in the first instance) by elimination of H^2O , and interchange between the group NH^2 and an OH -group; thus:



Amidoglyoxylic acid is similar in constitution to aldehyde-ammonia, $\text{CH}(\text{NH}^2)\text{OH}-\text{CH}^3$, the CH^3 being replaced by carboxyl.

This view of the constitution of the compound obtained by neutralising glyoxylic acid with ammonia receives some support from the fact that a compound exhibiting both acid and basic properties is obtained in like manner by decomposing calcium glyoxylate with oxalate of aniline. The substance thus produced is non-crystalline, dissolves easily in ammonia, and is likewise soluble in hydrochloric acid; and the solution, when evaporated, leaves a soluble hydrochloride from which a platinumchloride may be prepared.

Debus, on the other hand (ii. 922), maintains that the ammonia-derivative of glyoxylic acid is a true ammonium salt, inasmuch as it is formed from calcium glyoxylate by the ordinary process of double decomposition, and yields silver glyoxalate by decomposition with silver nitrate.* The acidity of the evaporated salt he attributes to the partial loss of ammonia, which is constantly observed in the evaporation of solutions of ammonium salts (p. 75). He therefore still considers that glyoxylic acid is correctly represented by the formula $\text{C}^2\text{H}^2\text{O}^3$, which is likewise most in accordance with the fact that glyoxylic acid is formed by direct oxidation from glyoxal, $\text{C}^2\text{H}^2\text{O}^2$.

Reactions.—1. When hydrochloric acid is added to a mixture of syrupy glyoxylic acid and hydrocyanic acid, and the mixture is set aside for some weeks, crystals of sal-ammoniac separate, and the solution, if then agitated with ether, yields a small quantity of oxalic acid; and on evaporating it to dryness at 100° and extracting the residue with absolute alcohol and ether, a solution is formed containing glycollic acid. 2. When a dilute aqueous solution of glyoxylic acid is agitated with silver oxide, and hydrogen sulphide is passed into the liquid, there is obtained, together with oxalic acid, a syrupy sulphuretted acid which is but partially precipitated by lead acetate, and may thus be separated from the oxalic acid. The solution of its potassium salt forms precipitates with lead acetate, mercuric chloride, and barium chloride. The acid is easily etherified. It probably consists of 'mercaptan-glycollic acid' [? thioglycollic acid]. 3. Glyoxylic acid is strongly acted upon by *acetic anhydride*, and *sodium acetate* (Perkin's reaction), but neither fumaric nor maleic acid could be discovered in the dark-coloured product, the only substances present, besides glycollic and oxalic acids, being a dark-coloured syrupy compound having an odour of burnt sugar (Böttiger, *Deut. Chem. Ges. Ber.* x. 1084).

GMELINITE. This mineral occurs in Nova Scotia in two distinct types, the first of which, occurring at Two Islands and Cape Blomidon, exhibits $+\text{R}$ and $-\text{R}$ almost in equilibrium, together with ∞R , 0P , and $\infty\text{P}2$. The prism ∞R is horizontally striated; $\infty\text{P}2$ has somewhat rounded edges, and the colour is light flesh-red to milk-white. The second type occurs on the Five Islands, eight miles distant from Two Islands. In this type there is an entire absence of 0P ; $-\text{R}$ is scarcely discernible, ∞R exhibits a strong lustre on its faces without a trace of striation. The characteristic form of this locality is -2R , which is distinctly striated parallel to its combination-edges with R , the crystals being complete rhombohedrons, some faces being well developed, whereas other crystals, when small, exhibit drusy faces. Colour darker than in the crystals of the first type. Gmelinite from Bergen Hill occurs in a type intermediate between the two already described, as R and $-\text{R}$ are unequally developed, and 0R and $\infty\text{P}2$ are not present. Chemical composition as follows:

	SiO^2	Al^2O^3	Fe^2O^3	CaO	Na^2O	K^2O	H^2O
Two Islands	51.36	17.81	0.15	5.68	3.92	0.23	20.96 = 100.11
Five Islands	50.45	18.27	0.17	1.12	9.79	0.20	20.71 = 100.71
Bergen Hill	48.67	18.72	0.10	2.60	9.14	—	21.35 = 100.58

From the above analyses it is evident that the chemical composition exerts a considerable influence upon the crystallographical type. Gmelinite from Five Islands contains a large amount of soda, and has a rhombohedral type, R predominating; that from Bergen Hill exhibits no particular characteristics, whilst that from Two Islands,

* It must be observed, however, that Perkin does not deny the formation of ammonium glyoxylate in the first instance, or its existence in solution, but considers that this salt is converted into an amido-compound by loss of H^2O , on evaporation in the manner above described.

in which there is a large proportion of limo, is remarkable for its pyramidal character (Howe, *Sill. Am. J.* [3], xii, 270).

GNEISS. The sp. gr. and amount of silica in a series of varieties of gneiss in the Black Forest of Baden have been determined by Vogelgesang (*Jahrb. f. Min.* 1873, 431):

1-6. Gneiss from the neighbourhood of Zindelstein, 9 kilom. W.N.W. of Donau-echingen: 1. Ordinary gneiss. 2. Porphyritic. 3. Fine-veined, resembling mica-slate. 4. Brown porphyritic. 5. Red granular-veined. 6. Thin, scaly gneiss, resembling hornblende. 7 and 8. Gneiss from Unterkirnach, 8 kilom. W.N.W. of Villengen. 7. Coarse-veined gneiss. 8. Granular-veined, imbedded in the preceding in layers from 1.5 to 2 meters thick:

	1	2	3	4	5	6	7	8
Sp. gr. . .	2.708	2.724	2.712	2.685	2.617	2.769	2.725	2.650
SiO ₂ per cent.	55	56	59	63	65	53	56	75.3

The first three varieties, after several days' treatment with cold dilute sulphuric acid, yielded, in solution, the following quantities of substance:

1. = 23.64 2. = 14.84 3. = 23.48 per cent.

The last acid extract contained 6 per cent. SiO₂, 6 per cent. Fe₂O₃, 5 per cent. Al₂O₃, together with the greater part of the CaO, MgO, and alkalis present in the rock, therefore nearly half its amount of bases, but only about $\frac{1}{10}$ of the amount of the silica present. The analysis of rock No. 4 gave:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Alkalis	Loss by ignition
63.34	15.44	11.89	2.93	1.76	3.36	1.29 = 100.01.

A petrographic description of the gneiss of Sweden has been given by A. E. Törnbohm (*Jahrb. f. Min.* 1874, 131). P. Schweitzer (*Am. Chem.* iv, 443) has analysed the quartz, feldspar, and mica of the granitic gneiss on which New York is built. (See also *Jahresb. f. Chem.* 1874, 1244, 1250, 1258.)

On the Heat-conductivity of Gneiss, see HEAT.

On Gneiss-granulite, see GRANULITE.

GOETHITE. This variety of ferric oxide is found in Adair County, Missouri, in cavities of calcite concretions, forming crystals from $\frac{1}{8}$ to $\frac{3}{4}$ inch long, aggregated in bundles at the base of the calcite from which they radiate. Sometimes a single crystal shoots directly through a calcite crystal. Sometimes also a quartz crystal is seen penetrated in various directions by goethite. Minute, velvety balls of goethite, not larger than $\frac{1}{10}$ of an inch, are also found resting on the calcite (Broadhead, *Sill. Am. J.* xiii, 419).

GOLD. *Occurrence.*—Gold in a state of fine crystallisation is found at Vöröspatak. The predominating forms are O and $\infty O\infty$, often in equilibrium, with occasionally 303 and ∞O and $\infty O2$ in combination, but the cube generally predominates. A twinning appears to be general, occurring even with gold in the form of 'plate' and 'foil.' The faces of $\infty O\infty$ are also often characterised by a fine double striation parallel to the cubical edges, also the combination-edges of $\infty O\infty$ with O. The octohedral faces generally exhibit an equilateral striation, and depressions are sometimes observed on the cubical faces. The largest crystals found in this locality measured from 12 to 15 mm. Twins of the 'middle crystal' are characterised by an abnormal development parallel to the combination-edge between O and $\infty O\infty$, whilst twins of the form $\infty O2$ are curtailed in the direction of a triangular axis, and have the appearance of a very regular obtuse hexagonal pyramid. Gold occurs also at Vöröspatak acicular, and as 'wire,' and crystals which at first sight appeared to be prisms, were found in reality to be peculiar 'penetration-twin' cubes, with $\infty O2$ in combination. The plate and foil formations are produced by twinning with an abnormal development parallel to a face of the octohedron (G. vom Rath, *Jahrb. f. Min.* 1876, 866).

In Idaho (U.S.), gold occurs in scheelite, intimately associated with small quantities of pyrites, chalcopyrite, and leucopyrite. In the Golden Queen Mine, Lake Co. Colorado, gold occurs in scheelite in small crystalline granules, filling what appears to have been a geode of scheelite crystals (B. Silliman, *Sill. Am. J.* xiii, 451).

E. Cohen (*Jahrb. f. Min.* 1873, 511) describes the occurrence of gold at Marabastad and Eersteling in South Africa. The gold is diffused through quartz-veins in metamorphic slate, whereas the quartz-veins in the granite appear to be free from it. In the secondary beds the gold is very widely diffused, but seldom occurs in large quantities in any one place. In Mindano, one of the Philippine Islands also, gold is rarely found in quartz-veins, but mostly in secondary strata, accompanied by platinum, lead (?), magnetic iron ore, specular iron ore and zircon (Minard, *Bull. Soc. Chim.* [3], ii, 403).

Specimens of native gold have been analysed by A. H. Church (*Chem. News*, **xxix.** 199, 209; **xxxi.** 153): *a.* From Ladock in Cornwall; *b.* Ashantee gold; *c.* Gold from Wanlockhead in Scotland; *d.* From Sutherlandshire:

Au	Ag	Cu	Fe	SiO ² and loss	Sp. gr. at 16°
92.34	6.06	—	trace	1.60 = 100	—
90.055	9.940	trace	trace	= 99.995	17.55
88.60	12.39	—	0.35	= 99.34	16.50
79.22	20.78	—	—	= 100	16.62

Analyses by R. Smith of gold from Queensland: (*a*) from Gilbert River, (*b*) from Paddy's County, have been published by R. Daintree (*Geol. Soc. J.* **xxviii.** 297):

Au	Ag	Cu	Pb	Bi	Fe	
89.920	9.688	0.128	0.026	—	0.070	= 99.832
92.800	6.774	0.048	0.048	trace	0.014	= 99.684

The following samples obtained by melting gold direct from the mines have been analysed by S. Kern (*Chem. News*, **xxxvii.** 23).

	1	2	3	4	5
Gold	99.46	99.280	98.50	94.20	96.75
Silver	0.52	0.640	1.48	5.76	3.17
Lead	traces	0.005	traces	0.01	0.01
Copper	0.01	0.070	0.01	0.01	0.06
Bismuth	0.01	0.005	0.02	—	—
Iron	—	—	—	traces	none

No. 2 could be hammered in the cold, but fell to pieces when being forged in a heated condition. Specimen plates from these alloys tore easily, and were very brittle. Ingots prepared from them after they had been worked with nitric acid and refined by cupellation, showed no brittleness, forged well, and were free from lead, bismuth, and iron. These results confirm the experiments of Roberts as to the effect of lead, antimony, and bismuth, in imparting brittleness to gold. Gold containing notable traces of arsenic showed no brittleness; but 0.05 to 0.08 per cent. of arsenic was found to prevent gold being readily worked under the hammer.

Preparation.—On the separation of the gold (about 18 per cent.) contained in the silver chloride formed in the purification of argentiferous gold by means of chlorine gas (1st Suppl. 652), see 2nd Suppl. 575.

On the separation of gold from silver, and the preparation of fine gold, as practised in the Assay Office at Frankfort-on-the-Maine, see H. Rössler (*Liebig's Annalen*, **clxxx.** 240; *Jahresb. f. Chem.* 1876, 285).

For recovering the small quantities of gold remaining in baths which have been used for electro-gilding, Böttger boils the liquid with a strongly alkaline solution of sodium stannite, whereby a velvet-black precipitate is formed containing gold and tin. This precipitate is washed and dissolved in the smallest possible quantity of aqua regia, and from this solution the gold is precipitated in the metallic state by acid sodium tartrate (*Deut. Chem. Ges. Ber.* 1876, 285).

W. Skeay finds, contrary to the statement of Daintree (2nd Suppl. 574), that when a piece of gold is immersed in a solution of auric chloride, and an organic substance, such as wood or cork, is likewise introduced into the liquid, only a small quantity of gold is precipitated on the immersed metal (*Chem. News*, **xxx.** 162).

For the preparation of precipitated gold (for gilding on porcelain, &c.), P. Weisskopf (*Dingl. pol. J.* **ccx.** 65) recommends the following process. To 750 c.c. of a slightly acid solution of auric chloride are added 12 grams of commercial caustic soda dissolved in 200 c.c. water, 0.5 gram starch or milk sugar dissolved in 6 c.c. water, and then 6 c.c. alcohol of 80 per cent. and 6 c.c. aldehyde. The gold is thereby precipitated in the form of a black powder, becoming cinnamon-brown when washed, and finer and softer than that which is obtained when ferrous sulphate is used as the precipitant.

On the Electrodeposition of Gold, see ELECTROLYSIS (p. 711).

Detection and Estimation.—According to S. Kern (*Chem. News*, **xxxii.** 171), potassium thiocyanate is an extremely delicate test for gold. The gold is first separated from foreign metals, and then converted by addition of sodium chloride into NaAuCl₄. On adding this solution to the thiocyanate, an orange-red turbidity is produced, and soon afterwards a precipitate of the same colour. On slightly warming the liquid, however, this precipitate disappears, and the liquid becomes quite colourless.

To detect gold in iron pyrites, H. Schwarz (*Dingl. pol. J.* **ccxviii.** 212) fuses 100 grams of the powdered mineral with 46.6 grams of iron filings under a layer of common salt. When cold the fused mass is broken up, and the resulting ferrous sulphide

dissolved in dilute sulphuric acid. The solution being filtered off, the residue containing the sulphide of gold is washed, dried, and roasted on a tile; some borax and 2 grams of pure lead are then added, and the mixture fluxed in a muffle furnace; a small button of lead is thus obtained, in which, after dissolving in aqua regia, the presence of gold can be easily recognised by the usual tests.

For the gold-assay of pyrites in Australia, a kilogram of the mineral is roasted dead, and stirred up with water to a stiff paste; a spoonful of mercury is then added, and the whole triturated in an iron mortar; and after a while another equal quantity of mercury is added. The mixture is then treated with hot water, sodium carbonate, and 5 or 6 spoonfuls of mercury, again triturated for some time, and the amalgam is levigated, collected, and distilled. This process yields from 80 to 90 per cent. of the quantity of gold that is obtainable by assaying in the dry way (G. Ullrich, *Dingl. pol. J.*, cxxvii. 517).

Gold-amalgams. The liquid amalgams obtained by squeezing alloys of gold and mercury through chamois-leather always contain (at the ordinary temperature) 0.126 per cent. of gold. At 0° the proportion is 110 percent. gold; at 20°, 126 per cent.; and at 100°, 650, per cent.: these amalgams, therefore, behave like aqueous solutions. When glass capillary tubes are used instead of chamois-leather for the separation of the liquid amalgam, no relation can be discovered between the diameter of the tube and the percentage of gold.

The residues left after the action of nitric acid on solid or liquid gold amalgams are not homogeneous, which proves that there probably exist definite compounds of gold and mercury dissolved in excess of mercury, just as in aqueous solutions definite hydrates are mixed with excess of water (Kasantseff, *Bull. Soc. Chim.* [2], xxx. 20). A mixture of gold and mercury heated to a temperature a little above the boiling point of mercury till its weight became constant, left an amalgam containing 16.02 to 10.5 per cent. mercury, which is the composition of the compound Au^3Hg (Schnauss, *Arch. Pharm.* [3], vi. 411).

Bromides (J. Thomsen, *J. pr. Chem.* [2], xiii. 337). The *monobromide*, or *Aurous Bromide*, AuBr , may be prepared by heating hydro-auric bromide, AuHBr^4 , in a porcelain dish, in such a manner that the heat may affect the bottom and not the sides. Water and hydrogen bromide then escape, and a solid mass is left consisting chiefly of the tribromide; and this, when heated for some hours at about 115°, with occasional stirring, gives off bromine and a little hydrogen bromide, and finally leaves a yellowish-grey greasy mass having the composition AuBr . This bromide is a yellowish-grey, friable, greasy substance, permanent in the air, resolved at a temperature a little above 115° into bromine and gold, and converted by hydrobromic acid into gold and hydro-auric bromide: $3\text{AuBr} + \text{HBr} = \text{Au}^2 + \text{AuHBr}^4$.

The *tribromide*, or *Auric Bromide*, AuBr^3 , is best prepared by acting on hydro-auric bromide with ether in a flask in which the liquid may be cooled by exhausting the air. A drop exposed on a glass plate till the ether has evaporated shows under the microscope a dark, very fine layer of regular crystals. In preparing large quantities of the bromide, the concentrated solution must be evaporated at a very low temperature. Auric bromide forms a dark-brown powder which is anhydrous and not deliquescent. It is perfectly soluble in water and ether, and the solutions are almost black when concentrated. An aqueous solution of auric bromide is easily prepared by shaking auroso-auric bromide for some time with warm water. A solution of auric bromide is reduced by sulphurous acid, first to aurous bromide, and then to metallic gold, the strongly coloured solution being first completely decolorised without formation of a precipitate, and the colourless solution yielding with potassium iodide a precipitate of aurous iodide having a fine yellow colour. The second stage of the decomposition takes place after a few minutes only, gold being separated and the liquid again becoming coloured dark brown by reproduction of the tribromide.

Hydro-auric Bromide, $\text{AuHBr}^4 + 5\text{H}^2\text{O}$, is prepared by pouring bromine on pulverulent gold, and when the reaction is over, adding a quantity of hydrobromic acid (sp. gr. 1.38) equal in weight to the gold employed, and then as much bromine as is required to dissolve the gold completely. The solution left to itself at ordinary temperature soon deposits large, flat, needle-shaped crystals, having a dark cinnabarred colour; they melt in their water of crystallisation at 27°, but may be preserved without alteration at ordinary temperatures, either in the air or over lime or sulphuric acid.

The *dibromide*, or *Auroso-auric Bromide*, Au^2Br^2 , or $\text{AuBr}.\text{AuBr}^3$, formed by the action of bromine on finely divided gold, is a nearly black, brittle, non-deliquescent mass, which decomposes at 115° into the monobromide and free bromine. It dissolves slowly in water, with absorption of heat, and formation of aurous and auric bromides. It is more quickly decomposed by acids, and partially by anhydrous ether, auric

bromide being dissolved, while the residue, probably consisting chiefly of aurous bromide, decomposes slowly, leaving metallic gold.

Chlorides (Thomson, *loc. cit.*) The *monochloride*, or *Aurous Chloride*, AuCl , is formed by heating the trichloride to 185° , the completion of the change being indicated by the yellow colour of the product.

The *trichloride*, or *Auric Chloride*, AuCl_3 , is rapidly and easily prepared by decomposing auroso-auric chloride with a small quantity of water, the complete decomposition of the separated aurous chloride into auric chloride and gold being promoted by heating. On decanting the solution from the separated gold, evaporating it slowly, and finally drying the residue at 150° , the trichloride remains in the form of a dark brown crystalline mass. As dilute solutions of auric chloride are apt to decompose during evaporation, care must be taken to have the solution sufficiently concentrated; also to protect the sides of the basin from overheating. Auric chloride is also obtained as a bye-product, during the preparation of auroso-auric chloride, in the form of large, reddish brown, laminar crystals. It is very deliquescent in damp air, and very soluble in water, forming a dark red solution.

Hydrated Auric Chloride, $\text{AuCl}_3 + 2\text{H}^2\text{O}$, is formed when the solution of auric chloride, prepared as above, is concentrated by evaporation till a pellicle forms on the surface, and separates in large dark orange-coloured brittle crystals often grouped in tufts; they are very hygroscopic and deliquescent, but give off their water of crystallisation in dry air, even at ordinary temperatures.

The *dichloride*, AuCl_2 , or Au^2Cl_4 , or *Auroso-auric Chloride*, $\text{AuCl} \cdot \text{AuCl}_3$, is easily obtained by the action of dry chlorine gas on spongy gold (best prepared by precipitation with sulphurous acid, boiling with nitric acid, washing, and drying at 170°). It is a dark-red, hard body, easily reduced to a fine powder, very hygroscopic, and decomposed by water into aurous and auric chlorides, which may be separated from each other by rapid filtration; the aurous chloride, however, is decomposed by washing into chloride and metallic gold. The dichloride is decomposed at 250° , into chlorine and auric chloride, part of which volatilises in the rapid current of gas.

By acting on auric chloride with *silver fluoride*, F. W. Clarke (*Sill. Am. J.* [3], xiii. 291) has obtained a brown mixture of auric oxide and silver chloride, the gold fluoride probably formed in the first instance being decomposed by the water present into auric oxide and hydrofluoric acid.

Auric Hydroxide, AuHO^2 , or $\text{Au}^2\text{O}^3 \cdot \text{H}^2\text{O}$, is best obtained, according to Thomson, by heating a very dilute solution of auric chloride (about 1 mol. AuCl_3 to 800 mol. water) with 3 mol. sodium hydroxide—whereupon the liquid becomes first bright yellow and then dark brown—and adding a solution of sodium sulphate, which throws down the auric hydroxide in the form of a dark brown precipitate. It is insoluble in water, but dissolves easily in very dilute hydrobromic acid, less easily in very dilute hydrochloric acid (Thomson).

Sulphides. According to A. v. Schrötter and E. Privoznik (*Dingl. pol. J.* cxxiii. 360), it is not possible, with the materials and processes commonly used, to obtain definite compounds of gold and sulphur by precipitating gold-solutions with hydrogen sulphide, whether these solutions are acid or neutral, cold or hot, dilute or concentrated, the precipitates formed being almost always mixtures of a sulphide of gold with free gold or free sulphur. Neither can a definite sulphide of gold be obtained by dissolving the precipitated sulphide in a solution of the sulphide of an alkali-metal, because, when the solution thus formed is decomposed by an acid, the resulting precipitate is always mixed with free sulphur, which cannot be removed without decomposing the gold sulphide.

According to W. Skey (*Chem. News*, xxx. 36), gold sulphide is dissolved at ordinary temperatures by potassium cyanide, and is slowly attacked by mercury, with formation of mercury sulphide.

GOLD-BRONZE. Tungsto-potassic Tungstate. See TUNGSTATES.

GOMBO. The gombo (*Hibiscus syriacus*), a malvaceous plant cultivated in Syria and Egypt for the sake of its fruit, is also used for the manufacture of paper. The fibre is prepared for the purpose by mechanical treatment in running water, without the aid of any chemical process; and the paper produced from it is said to be equal in beauty and tenacity to the best rag paper (E. Landrin, *Compt. rend.* lxxix. 1132).

GRAHAMITE. This carboniferous mineral, originally found in Ritchie County, Virginia (1st *Suppl.* 653), occurs also in Mexico. In the Cristo mine in the north-western part of the State of Vera Cruz, it forms a vein between shales and a

roof connected with the vein and separating the shale from the overlying conglomerate; it is semigranular, cleavable, and separated in columns. An analysis by W. Wallace gave 62.14 per cent. of volatile matter, viz. 61.32 per cent. illuminating gas, 0.46 sulphur, and 0.36 water, and 37.36 per cent. coke, containing 31.36 carbon, 0.37 sulphur, and 5.86 ash. Both grahamite and albertite (a black shining mineral resembling cannel coal, from Albert County, New Brunswick), (*Chem. News*, vi. 182), appear to have been formed from petroleum by loss of hydrogen and assumption of oxygen (J. P. Kimball, *Sill. Am. J.* [3], xii. 277).

GRAMMATITE. See HORNBLENDE.

GRANITE. The following nomenclature for the several varieties of granite rocks is proposed by H. Rosenbusch (*Zeitschr. geol. Ges.* xxviii. 369; *Jahrb. f. Min.* 1877, 544); *Muscovite granite*, composed of quartz, orthoclase, plagioclase, potash-mica; *Granitite*: quartz, orthoclase, plagioclase, magnesia-mica; *Amphibole or Hornblende granite*: quartz, orthoclase, plagioclase, hornblende; *Granite*: quartz, orthoclase, plagioclase, potash-mica and magnesia-mica; *Hornblendiferous granite* or *Amphibole granite containing magnesia-mica*: quartz, orthoclase, plagioclase, magnesia-mica or hornblende. *Porphyritic granites* not unfrequently contain pyroxene.

Rosenbusch also describes the transitions of structure from granite, especially hornblende-granite, to quartz-porphry, and gives the composition of two extreme varieties, from the Vosges, analysed by Unger:

(1). Typical variety of granite from the Andlauthal below Hohwald. (2). Porphyritic variety from the Kirneckthal near Fontaine Laquante:

	SiO ²	Al ² O ³	Fe ² O ³	FeO	CaO	MgO	K ² O	Na ² O	H ² O	
(1).	71.785	17.518	2.279	1.026	1.892	0.778	2.890	2.045	0.818	= 101.03.
(2).	68.629	17.184	3.586	0.204	2.414	1.111	3.667	2.110	1.066	= 99.971

On the relation between Granitic and Porphyritic structure, and on the genesis of Granite, see also K. A. Lossen (*Jahrb. f. Min.* 1875, 542).

On the Granite-porphyrises of Saxony, see PORPHYRY.

On Enclosures of Granite in the Volcanic Tufas of the Swabian Alps, see Deffner (*Jahresh. f. Chem.* 1873, 1210).

On the Granite of Barr-Andlau, see Unger (*Jahrb. f. Min.* 1876, 755; *Chem. Soc. Jour.* 1877, ii. 416).

On the Granite-veins of the Granulite mountains of Saxony, see Credner (*Jahrb. f. Min.* 1875, 751; *Chem. Soc. Jour.* 1876, i. 198).

Action of Carbonic Acid Water on Granite.—Pavesi a. Rotondi (*Deut. Chem. Ges. Ber.* vii. 818) have examined the action of water containing carbonic acid on granite, by means of comparative analyses of the nucleus and decomposed crust of old moraine-blocks from the neighbourhood of Como. The specimens were taken from a depth of 8 meters. (1). Unaltered nucleus. (2). Decomposed crust:

	Soluble in HCl	CO ²	Fe ² O ³	Al ² O ³	CaO	
(1).	25.60	2.43	1.99	66.91	3.21	= 100.14
(2).	96.54	—	3.45	—	—	= 99.99

GRAPES. From experiments on the ripening of grapes by C. St. Pierre and L. Magnier (*Compt. rend.* lxxxvi. 401), it appears that, as the grapes approach maturity, they evolve carbon dioxide both in the dark and in daylight, this evolution taking place indifferently in air or in any inert gas. When the observation is carried on for a sufficient length of time, the quantity of carbon dioxide evolved is always found to be greater than that of the oxygen consumed. Grapes absorb or give off moisture accordingly as they are kept in damp or in dry places. As maturity approaches, the acids diminish and the quantity of sugar increases. The mechanism of ripening appears to be the following: The acids and glucose are formed in the plant and carried by the sap to the grape, where the acids are destroyed while the sugar becomes concentrated. When the grapes become over-ripe, the sugar is also consumed.

Ripening of Grapes removed from the Vine.—Experiments have been made by Pollacci (*Gazz. chim. ital.* 1877, 517) to determine whether the process of ripening in sour grapes continues after they are separated from the vine. The mode of experimenting consisted in taking bunches of sour grapes, dividing them as equally as possible both as to state of maturity, size, &c. of the grapes, and the weight; then estimating the glucose and the acid in one portion of the grapes just after gathering, and the same in another portion after the lapse of ten or twelve days, the grapes having been kept in the shade. In every instance the amount of glucose had increased while that of the acid had diminished; this effect was still more marked when the grapes were exposed to sunshine. These results show that grapes gathered whilst unripe continue

to ripen; the action, however, ceases after a certain time, so that the grapes never become fully ripe.

GRAPHITE. According to G. vom Rath (*Jahrb. f. Min.* 1874, 521), graphite occurs, partly massive, partly as a coating from 0.2 to 0.5 mm. thick, on calc spar, in fissures of a Middle Devonian limestone in the district of Wildewiese, Upper Rhrthal, Westphalia. A graphite containing 64.02 per cent. carbon, 21.13 ash, and 4.8 water occurs, together with iron pyrites and brown hematite, near Dobschau in Hungary. It is easily incinerated in contact with the air, in which respect it resembles anthracite; it might therefore be called *graphite-anthracite* (K. John, *Verh. geöl. Reichsanstalt.* 1874, 245).

Several specimens of graphite from Rottenmann in Styria have been examined by C. v. Hauer and C. John (*ibid.* 1875, 159). They yielded 86.0, 27.4, and 26.5 per cent. ash relatively to 14.0, 72.6, and 73.5 per cent. carbon. In other samples (*ibid.* 161), the proximate constituents of the ash and the sulphur were determined, with the following results:

	Total ash	SiO ²	Fe ² O ³	Al ² O ³	CaO	S
1.	32.5	21.50	1.75	7.50	1.25	0.31
2.	60.9	27.50	5.00	25.50	2.50	0.24
3.	73.8	39.50	4.00	6.75	2.25	0.38
4.	53.2	33.50	11.50	5.75	2.50	trace
5.	24.9	17.00	3.50	3.25	trace	0.22
6.	60.0	39.50	7.24	11.75	1.50	0.38
7.	31.0	21.50	3.50	4.25	1.25	trace

Two specimens of graphite from the Stephanovsky Mine in Siberia have been analysed by S. Korn (*Chem. News*, xxxii. 229):

C	SiO ²	Fe ² O ³	Al ² O ³	CaO	MgO	Volatile matters	S
36.06	37.72	4.02	17.80	1.20	3.20	trace	= 100
33.20	43.20	3.05	15.42	1.06	4.03	0.04	= 100

At Mugrau in Bohemia, graphite occurs in long layers enclosed in gneiss, and in immediate contact with limestone. The formation is included in the district bounded on the east by Plaben and Krumau, and on the west by Winterberg, with a N.W.N. 'strike,' and an inclination of from 30°–80°. Most of the graphite from this locality is of good quality. The gneiss appears to be considerably decomposed in the immediate neighbourhood of the graphite vein, being in some cases, richer in iron, and occasionally passing into graphite-gneiss, the rock being thoroughly impregnated with graphite, and of a black colour. At the contact-zone of the graphite and limestone, the graphite is accompanied by calcite, chloropal (i. 921), and a new mineral called *ihleite* (q.v.)

Magnetic properties of Graphite.—The particles of iron carbide which are left behind when iron is dissolved in acids are magnetisable and become permanently magnetic. Of four pieces of native graphite examined, the most ferruginous, probably from Baireuth, exhibited diamagnetism between the poles of a powerful electromagnet; the other three were magnetic (A. L. Holz, *Pogg. Ann.* cli. 69).

On the Specific Heat of Graphite, see HEAT.

On the behaviour of Graphite at high temperatures, see CARBON (p. 404).

G. Rose found that laminar graphite is more difficult to burn than diamond—a statement confirmed by R. Blindow (*Deut. Chem. Ges. Ber.* ix. 19)—but that compact graphite burns more readily than diamond. When these several forms of carbon were heated in the muffle of an assay furnace, it was found that in the course of thirteen minutes there were burned: of laminar graphite, 27.45 per cent.; of diamond, 97.76; of compact graphite, 100 (*Berl. Acad. Ber.* 1872, 516).

Analysis.—For the valuation of graphite, Wittstein (*Dingl. pol. J.* ccxvi. 45) recommends the process used by Berthier for determining the value of a substance as fuel. 1 gram of the finely pulverised graphite is mixed with 25 grams of pulverised litharge; the mixture is introduced into an unglazed porcelain crucible, and covered with 25 grams of litharge; and the whole is slowly heated between the coals. 34 parts of reduced lead are equivalent to 1 part of carbon.

To determine the other constituents, 1 gram of the finely pulverised graphite is heated to low redness, and the loss of weight estimated as water, then fused with a mixture of sodium and potassium carbonate and a small quantity of solid potassium hydroxide, whereby a complete disintegration of the insoluble constituents, such as clay and quartz, is obtained. The loss of carbon consequent on the partial destruction of the graphite in this treatment has no essential influence on the result of the analysis,

inasmuch as the other constituents, as silica, alumina, ferric oxide, &c., can be estimated by weighing, and the final loss reckoned as carbon and added to the carbon directly obtained.

On the estimation of Graphite in Cast Iron, see IRON.

GRAPHITIC ACID. See CARBON (p. 403).

GREENSTONE. Analyses by G. Dietrich of two greenstones from the Adalbert Mine in Příbram, at the depth of 1000 meters, have been published by K. Vrba (*Jahrb. f. Min.* 1876, 137): (1). Fine-grained mixture of predominant plagioclase with augite, chlorite, quartz, and fragments of ore. Grains of calcite are regarded by Vrba as original constituents of the rock. Sp. gr. = 2.793. (2). Compact; poor in augite, which is almost wholly converted into chlorite. Sp. gr. = 2.857:

	SiO ²	Al ² O ³	Fe ² O ³	FeO	CaO	MgO	K ² O	Na ² O	CO ²
1.	58.82	10.17	5.05	7.12	10.27	4.00	0.68	2.55	1.47 = 100.13
2.	51.50	14.14	3.65	6.96	8.08	7.64	1.19	1.97	4.96 = 100.09

The greenstone of the Terraco Mine near St. Stephen's, Cornwall, contains scorodite, pharmacosiderite and olivenite in its hollows and clefts. The scorodite is mostly found in stellar groups of very small crystals, less frequently in rhombic pyramids of a bluish-green colour; the pharmacosiderite in small cubes and octohedrons of a deep green colour, and the olivenite in tabular crystals associated with scorodite (J. H. Collins, *Jahrb. f. Min.* 1876, 868).

On Greenstone Trachyte, see TRACHYTE.

GROUND PEA. *Arachis hypogaea.* The ash of this plant, cultivated in Virginia, has been analysed by W. S. Brown (*Chem. News*, xxiv. 147). In 100 parts of the pure ash—excluding ferric oxide, regarded as an accidental impurity—there were found:

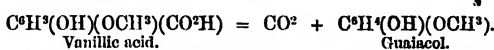
	Root	Stem	Leaves	Busk	Seed
K ² O	23.043	25.902	15.880	37.395	37.134
Na ² O	18.816	3.063	2.897	3.763	3.342
CaO	28.130	43.440	53.712	20.145	3.749
MgO	8.706	13.296	4.844	13.506	14.262
P ² O ⁵	3.684	1.590	4.679	5.062	29.102
SO ³	13.015	10.613	15.235	17.749	11.742
Cl	1.162	1.501	2.533	0.486	0.346
SiO ²	3.705	0.933	0.791	2.003	0.401
	100.261	100.338	100.571	100.109	100.078
Deduct O equivalent to Cl	0.261	0.378	0.571	0.109	0.078
	100.000	100.000	100.000	100.000	100.000

The total amounts of ash in the several parts of the dried plants were as follows:

Root	Stem	Leaves	Busk	Seed
11.830	13.288	7.747	2.586	1.818

Oil = 47.34 per cent. Nitrogen = 3.415 per cent.

GUAIACOL, C⁸H⁸O². This compound is formed by the distillation of calcium vanillate (p. 291) with slaked lime:



GUAIACUM. The *Resina Guajaci peruviana aromatica*, used in perfumery, has been examined by A. Kopp (*Arch. Pharm.* [3], ix. 192). By distillation with water, it yielded 4 per cent. of a yellow volatile oil, having an odour recalling those of peppermint and lemons, and yielding by repeated fractionation a portion which boiled between 167° and 168°, and had the composition C¹⁰H¹⁶. By fusion with potassium hydroxide, the resin yielded protocatechuic acid, together with other products; and by treatment with strong nitric acid, a nitro-compound, C²²H³⁴N²O¹⁰. The resin, previously freed from the volatile oil, yielded, by dry distillation, a brown oil, from which, by fractionation, a deep blue oil was obtained, boiling at 285°–290°, and having the composition C²⁰H³⁰O. By distillation over sodium, this blue oil yielded a colourless oil having the composition C²⁰H³⁰.

The statement of Hadelich (ii. 947) that the blue coloration of guaiacum, under the influence of oxidising agents, is due to the guaiaconic acid contained in it, has been confirmed by E. Schär (*Vierteljahrsschrift pr. Pharm.* xxii. 68).

GUANAJUATITE. A selenide of bismuth, from Guanajuato in Mexico, first noticed by Castello in 1873 (*Jahrb. f. Min.* 1874, 225), who regarded it as a sulpho-selenide of bismuth. It was afterwards analysed by Fernandez (*Sill. Am. J.* [3], xiii. 319), who regarded it as essentially a selenide of bismuth, and by Rammelsberg, who found it to contain 16.7 per cent. selenium and 65.4 bismuth, and suggested the presence of zinc (*Dana's Mineralogy*, 3rd Appendix, p. 22). This mineral was more fully examined by Frenzel (*Jahrb. f. Min.* 1874, 679), who assigned to it the composition 24.13 per cent. selenium, 6.60 sulphur, and 67.38 bismuth, leading to the formula $2\text{Bi}^2\text{Se}^3.\text{Bi}^2\text{S}^2$. Finally it has been analysed by J. W. Mallet (*Sill. Am. J.* [3], xv. 294), who found, in a specimen not quite free from argillaceous gangue:

Se	S	Bi	Al^2O^3	Fe^2O^3	SiO^2	H^2O	
31.64	0.61	59.92	2.53	trace	3.47	1.46	= 99.63.

The gangue is said to consist of galapelite (halloysite); and if the amount of this mineral present be calculated from that of the alumina, the composition of the specimen analysed will be:

Guanajuatite	Halloysite	Quartz	Moisture	
92.17	6.72	0.56	0.18	= 99.63

and the guanajuatite in the pure state will be found to consist of:

Se	S	Bi	
34.33	0.66	65.01	= 100

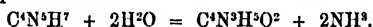
leading to the formula of a *sesquiselenide of bismuth*, Bi^2Se^3 , in which a small portion of the selenium is replaced by sulphur.

The physical characters of the mineral, as described by Frenzel, are as follows: Lustre metallic. Colour lead-grey. Streak highly lustrous. Mohl. Hardness = $2\frac{1}{2}$ –3. Sp. gr. = 6.25 at 21°. Occurs in compact masses having a fine-grained, laminar to fibrous structure; also in prismatic crystals, probably orthorhombic, exhibiting the brachypinacoid $\infty \text{P} \infty$, but no end-faces; they are for the most part indistinctly developed, in consequence of deep vertical striation. Cleavage distinct parallel to $\infty \text{P} \infty$.

Before the blow-pipe the mineral fuses, gives off a strong odour of selenium, and colours the flame blue. Fused with potassium iodide, it yields a fine red deposit of bismuth sulphide.

GUANAMIDE, $\text{C}^4\text{N}^3\text{H}^3\text{O}^2 = \text{H}^3\text{C}-\text{C} \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH}$ (Nencki, *Deut. Chem. Ges.*

Ber. ix. 232). A compound formed by heating 1 part of methyl-guanamino to 150° with 2 parts of strong sulphuric acid:



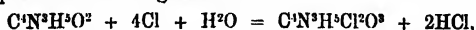
On mixing the cooled liquid with absolute alcohol, a bulky precipitate is thrown down; and on dissolving this precipitate in water, separating the sulphuric acid from the solution, evaporating the liquid to dryness, and treating the residue with concentrated hydrochloric acid, guanamide hydrochloride, $\text{C}^4\text{N}^3\text{H}^3\text{O}^2.\text{HCl}$, is obtained in needles.

Guanamide separated from this salt is very soluble in water, acids, and alkalis, slightly soluble in alcohol, and crystallises from a hot alcoholic solution in small rhombic needles. By mixing the concentrated aqueous solution of the hydrochloride with an alcoholic solution of platinic chloride, and leaving the liquid to evaporate over sulphuric acid, the *platinochloride*, $(\text{C}^4\text{N}^3\text{H}^3\text{O}^2.\text{HCl})^3.\text{PtCl}_4$, is obtained in yellow druses of concentric needles.

Guanamide treated with 5 or 6 parts of nitric acid, sp. gr. 1.3, is oxidised, with violent reaction, to cyanuric acid:



Dichloroguanamidine, $\text{C}^4\text{N}^3\text{H}^3\text{Cl}^2\text{O}^3$, is formed by the action of chlorine on a concentrated aqueous solution of guanamide:



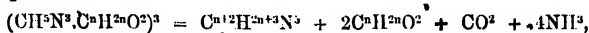
and separates in dazzling white anhydrous crystals. It is insoluble in cold, slightly soluble in hot water, soluble also in soda-ley, and is precipitated therefrom in great part by hydrochloric acid. By prolonged boiling with water, and more quickly by heating with alkalis, or by the action of sodium-amalgam in aqueous solution, it is resolved into cyanuric acid and a body smelling like chloroform, probably methylene chloride. Dichloroguanamidine is completely decomposed at 140°.

Tribromoguanamidine, $\text{C}^4\text{N}^3\text{H}^3\text{Br}^3\text{O}^3$, is produced by the action of bromine, on a warm aqueous solution of guanamide. It forms microscopic crystals, insoluble

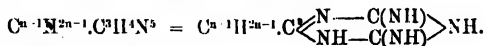
in water, alcohol, and ether. By boiling with water it is quickly resolved into cyanuric acid and bromoform :



GUANAMINES, $C^{n+1}H^{2n+3}N^3$ [$n = 1, 2, 3$, &c.], (M. Nencki, *Deut. Chem. Ges. Ber.* vii. 775, 1584; ix. 228, 232, 244). A series of bases produced by the action of heat on the guanidine-salts of the fatty acids. Their formation is represented by the general equation,



and their constitution may be represented by the formula



The following have been obtained :

Guanamine, $C^3H^6N^3 = H.C^3H^4N^3$.

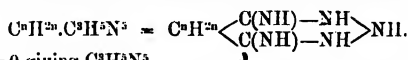
Methyl-guanamine, $C^4H^7N^3 = CH^3.C^3H^4N^3$.

Propyl- and isopropyl-guanamine, $C^6H^{11}N^3 = C^3H^7.C^3H^4N^3$.

Butyl-guanamine, $C^7H^{13}N^3 = C^4H^9.C^3H^4N^3$.

Pentyl-guanamine, $C^8H^{15}N^3 = C^5H^{11}.C^3H^4N^3$.

Nencki originally represented the guanamines by the general formula.—



$n = 0$ giving $C^3H^5N^3$

$n = 1$ „ $C^4H^7N^3 = CH^2.C^3H^5N^3$ (methylene-guanamine).

$n = 3$ „ $C^6H^{11}N^3 = C^3H^6.C^3H^5N^3$ (propylene-guanamine).

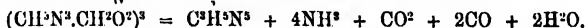
&c. &c.

The second term, $C^4H^7N^3$, which was the earliest obtained, was at first called *guanamine*; afterwards, when its lower homologue, $C^3H^6N^3$, was discovered, this latter was named *formoguanamine*, and the second term *acetoguanamine*, to indicate their production from formate and acetate of guanidine respectively. Subsequently the names *methylene-guanamine*, *propylene-guanamine*, &c., were adopted to indicate the formation of the several terms of the series from the first, $C^3H^5N^3$, by addition of CH^3 , C^2H^5 , C^3H^7 , &c.

The representation of the guanamines by the general formula $C^{n+1}H^{2n+3}.C^3H^4N^3$ ($n = 0, 1, 2, 3$, &c.), or $C^{n+1}H^{2n+3}.C^3H^4N^3$ ($n = 1, 2, 3$, &c.) above given, was proposed by Weith (*Ber.* ix. 458) and afterwards adopted by Nencki (*ibid.* 1013); and in accordance with this mode of representation, it is better to designate the first term of the series $C^3H^5N^3$ as *guanamine*, and the higher terms, as *methyl-*, *propyl-*guanamine, &c., accordingly as they are derived from the first by substitution of CH^3 , C^2H^5 , C^3H^7 , &c., for an atom of hydrogen.

Guanamine, $C^3H^6N^3 = H.C^3H^4N^3 = HC \begin{matrix} N \\ \diagup \quad \diagdown \\ NH-C(NH) \end{matrix} > NH$. *Formoguanamine*.

This base is produced by the action of heat on guanidine formate :

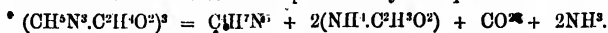


The carbon monoxide and water result from the decomposition of formic acid produced in the first instance (see the general equation above given). The heat must be raised to 200° , and kept at that point as long as crystals continue to separate; the liquid is then left to cool, and mixed with an equal volume of cold water; the undissolved base taken up by hot water, and converted by addition of a concentrated solution of oxalic acid into the oxalate; and this salt is decomposed by potash, which throws down the base in white rhombic needles.

Guanamine is a weak base, easily soluble in hot water, slightly soluble in alcohol, separating from water in anhydrous crystals, and melting at 350° . Its salts crystallise readily.

Methyl-guanamine, $C^4H^7N^3 = CH^3-C^3H^4N^3$. *Acetoguanamine*, *Methylene-guanamine* (originally called *guanamine* by Nencki). To prepare this base, dry guanidine acetate is submitted to fractional distillation on a sand-bath, whereupon it melts to a pale yellow liquid. As the temperature rises, a little water and acetic acid distil over, ammonia in abundance is evolved; and the boiling liquid ultimately attains a temperature of 228° – 230° , at which it remains constant. After being kept at this temperature for a quarter of an hour, it is allowed to cool, and the melted mass is exhausted with a little hot water. A small amorphous residue is then left, while the greater part of the mass dissolves in the water, forming a solution which on cooling

solidifies to a jelly consisting of methyl-guanamine acetate; and this, when freed from adhering liquid by filtration and pressure, and decomposed by dilute potash or soda, yields the free base. The reaction is represented by the equation—



The water, which is likewise given off, results from conversion of the ammonium acetate into acetamide.

Methyl-guanamine dissolves easily in alcohol, sparingly in cold, freely in hot water, and crystallises therefrom, when quickly cooled, in small nacreous, laminae; but by slower cooling it may be obtained in large laminated crystals often several centimeters long, or in needles belonging to the orthorhombic system. The crystals contain water, which they give off when dried in the air. Methyl-guanamine is destitute of taste and smell; it is not poisonous, and passes through the animal organism almost without alteration. It melts at 265° , and sublimes partly without decomposition.

Methyl-guanamine is a weak base, forming crystallisable compounds with acids and with salts. The *hydrochloride*, $\text{C}^6\text{H}^5\text{N}^3\cdot\text{HCl} + 2\text{H}^2\text{O}$, crystallises in monoclinic prisms and plates easily soluble in hot water. The *platinochloride*, $(\text{C}^6\text{H}^5\text{N}^3)^2\cdot 2\text{HCl}\cdot\text{PtCl}_4$, is a yellow crystalline precipitate, easily soluble in water, sparingly in alcohol. The *nitrate*, $\text{C}^6\text{H}^5\text{N}^3\cdot\text{NO}^3\text{H}$, crystallises in thick, anhydrous, monoclinic prisms, easily soluble in water. The dry salt decomposes when heated, with a slight explosion. The *argentonitrate*, $(\text{C}^6\text{H}^5\text{N}^3)^3\cdot\text{NO}^3\text{Ag}$, is formed by mixing a warm aqueous solution of the base with silver nitrate, and separates as an amorphous precipitate, the greater part of which redissolves when heated, and separates on cooling in rhombic plates. The *sulphate*, $(\text{C}^6\text{H}^5\text{N}^3)^2\cdot\text{SO}^4\text{H}^2 + 2\text{H}^2\text{O}$, crystallises from a warm acid solution in rhombic laminae, very soluble in water. The *acetate*, $\text{C}^6\text{H}^5\text{N}^3\cdot\text{C}^2\text{H}^3\text{O}^2$, prepared by heating acetate of guanidine and recrystallising, gives off acetic acid when dried at 100° .

Methyl-guanamine is readily oxidised by dilute *nitric acid*. With strong nitric acid it forms a yellow product, which is precipitated from a dilute solution by ammonia in amorphous flocks. By boiling with strong aqueous *potash*, methyl-guanamine is decomposed, with evolution of ammonia and formation of guanide, $\text{C}^6\text{H}^5\text{N}^3\text{O} = \text{C}^6\text{H}^5\text{N}^3 + \text{H}^2\text{O} - \text{NH}^3$. Heated with strong sulphuric acid, it is converted into guanamide, $\text{C}^6\text{H}^5\text{N}^3\text{O}^2 = \text{C}^6\text{H}^5\text{N}^3 + 2\text{H}^2\text{O} - 2\text{NH}^3$ (p. 900).

Propyl-guanamine, $\text{C}^6\text{H}^{11}\text{N}^3 = \text{CH}^3\cdot\text{CH}^2\cdot\text{CH}^2\cdot\text{C}^6\text{H}^5\text{N}^3$ (Nencki, *Deut. Chem. Ges. Ber.* ix. 228). This compound is obtained, like the preceding, by heating guanidine butyrate to 230° for about an hour, exhausting the slightly yellow fused mass with hot water, and treating the filtrate with strong soda-ley, which throws down the base as a white crystalline precipitate. For purification it is converted into the hydrochloride (whereupon a highly nitrogenised body separates in white flocks); this salt, after recrystallisation from alcohol, is decomposed by soda-ley, and the precipitated base is several times crystallised from hot water.

Propyl-guanamine crystallises by slow cooling or evaporation in four-sided rectangular plates, but when thrown down quickly from a hot solution, it separates in spherical crystalline groups or in hemihedral forms (sphenoids) with curved faces. It dissolves in 53.7 parts of water at 14.5° , and in 7 parts at 100° . It is precipitated from its aqueous solution by strong caustic soda, not by ammonia either from acid or from neutral solutions. It is easily soluble in alcohol. Heated in capillary tubes, it begins to sublime at 210° , and at 230° volatilises for the most part without melting, and leaves a slight yellow residuc. It dissolves in acids, forming well-crystallised salts, easily soluble in water and alcohol. The *hydrochloride*, $\text{C}^6\text{H}^{11}\text{N}^3\cdot\text{HCl}$, forms brilliant rhombic prisms and laminae, and contains $1\frac{1}{2}$ molecules of water of crystallisation which it loses in air. An *argentonitrate*, $\text{C}^6\text{H}^{11}\text{N}^3\cdot\text{NO}^3\text{Ag}$, which forms fine crystals, may be obtained by heating a concentrated aqueous solution with silver nitrate.

Isopropyl-guanamine, $\text{C}^6\text{H}^{11}\text{N}^3 = \text{CH}(\text{CH}^3)^2\cdot\text{C}^6\text{H}^5\text{N}^3$, prepared like the preceding, from isobutyrate of guanidine, crystallises from aqueous solution in pointed rhombohedrons resembling calcite, or in prisms with the two rhombohedrons aggregated in rows, as in quartz. It dissolves in 48.6 parts of boiling water, and in 176.7 parts of water at 18° ; in alcohol somewhat less easily than normal propyl-guanamine. It is distinguished from the normal base by being thrown down by ammonia from its solutions in strong mineral acids. *Nitrate of isopropyl-guanamine*, $\text{C}^6\text{H}^{11}\text{N}^3\cdot\text{NO}^3\text{H}$, crystallises in small tufts of concentric needles. The *argentonitrate*, $\text{C}^6\text{H}^{11}\text{N}^3\cdot\text{NO}^3\text{Ag}$, is more soluble in water than that of the normal base, and separates on evaporation over sulphuric acid, in prismatic crystals.

Butyl-guanamine, $\text{C}^8\text{H}^{13}\text{N}^3 = \text{C}^4\text{H}^9\cdot\text{C}^6\text{H}^5\text{N}^3$ (Bandrowski, *Deut. Chem. Ges. Ber.* ix. 240). Prepared by heating valerato (isopropylacetato) of guanidine.* Crystals

* At the same time an amorphous body is formed, quite insoluble in water, soluble in soda-ley and in the stronger mineral acids, and precipitated by organic acids.

lises in shining white rhombic needles, which sublime at 100° , melt at 172° – 173° , and resolidify at 127° . It dissolves somewhat sparingly in cold water, more easily in hot water, very easily in alcohol and ether. The crystals are anhydrous.

Butyl-guanamine is a very weak base. The acetate, which crystallises in tufts of slender needles, decomposes even on exposure to the air. The hydrochloride, $C^4H^{11}N^3.HCl$, separates from highly concentrated solutions in well-defined shining needles, very soluble in water. The sulphate, $C^4H^{11}N^3.SO^2H^2$, crystallises in small shining laminae. The argentonitrate, $C^4H^{11}N^3.NO^2Ag$, obtained by warming and filtering an aqueous solution of its components, crystallises in delicate, glistening, sparingly soluble needles, which turn brown when exposed to light.

The base treated with strong sulphuric acid was converted into a butyl-guanamido, $C^4H^{11}N^3O^2 = C^4H^9C \begin{smallmatrix} N-CO \\ \diagup \quad \diagdown \\ NH-CO \end{smallmatrix} NH$, oxidisable by nitric acid to cyanuric acid (probably together with butyl-isonitric).

Pentyl-guanamine, $C^6H^{13}N^3 = C^2H^{11}.C^3H^2N^3$ (*Amylene-guanamine*), is prepared from the guanidine salt of normal caproic acid, and may be obtained pure by precipitation from the hydrochloride. It forms shining, microscopic, quadratic pyramids, melts at 177° – 178° , and resolidifies at about 144° . The crystals are anhydrous, very slightly soluble in water, easily in alcohol. The hydrochloride crystallises in flat well-defined needles.

GUANIDE (bi-), $C^2H^2N^3$. See THIODICYANDIAMINES.

GUANIDINE, $CH^3N^3 = HN-C \begin{smallmatrix} NH^2 \\ \diagup \quad \diagdown \\ NH^2 \end{smallmatrix}$ *Formation and Preparation.*—1. By the action of heat on ammonium thiocyanate. When this salt is heated in an oil-bath to about 220° , ammonia and carbon disulphide are given off, and crystals of ammonium trithiocarbonate (Zeise's salt) sublime in consequence of a secondary decomposition.

The main reaction consists, first in the conversion of the ammonium thiocyanate into the isomeric compound, thiocarbamide (sulphurea), and secondly in the resolution of this compound into guanidine, ammonia, and carbon disulphide, according to the following equation:



The residue in the flask consists chiefly of guanidine thiocyanate, contaminated only with small quantities of ammonium thiocyanate and thiocarbamide; and from this salt the other salts of guanidine may be obtained by double decomposition (Delitsch, *J. pr. Chem.* [2], viii. 240; ix. 1).

According to Volhard (*J. pr. Chem.* [2], ix. 10), the conversion of ammonium thiocyanate into guanidine does not require a temperature higher than 170° , and at this comparatively low temperature the reaction appears to take place without formation of secondary products; it is necessary, however, to continue the heat for 100–120 hours; at about 180° – 190° , the same result is obtained in 20 hours. The residue in both cases consists mainly of guanidine thiocyanate, the yield being very satisfactory, and no gaseous product (such as CS^2 , &c.) being given off. Volhard regards the reaction as consisting, first, in the transformation of the ammonium thiocyanate into thiocarbamide, and secondly in the conversion of this compound, by loss of H^2S , into cyanamide, which, at the moment of its formation, unites with ammonium thiocyanate to form thiocyanate of guanidine: $CN^2H^2 + CNS.NH^4 = CN^3H^2.HCNS$. The formation of Zeise's salt is due to the combination of H^2S separated from the thiocarbamide with another portion of the ammonium thiocyanate.

Guanidine Thiocyanate purified by crystallisation from water or alcohol forms large flexible laminae having a peculiar fatty lustre; easily soluble in water and in alcohol; melting at 118° ; decomposing above 150° with evolution of ammonia, and leaving a residue of melam (Delitsch).

Guanidine Carbonate is obtained by mixing a solution of the thiocyanate with potassium carbonate (53 parts K^2CO^3 to 100 parts of the thiocyanate), evaporating down, and dissolving out the potassium thiocyanate with alcohol. Guanidine carbonate then remains, and may be freed from adhering potassium salt by recrystallisation from water (Volhard). It crystallises in trapez-hemihedral forms of the tetragonal system, and possesses the power of circular polarisation. The sulphate crystallises in the regular, the lactate in the orthorhombic system (Bodewig).

Guanidine carbonate heated to 100° with benzoic anhydride yields dibenzoyl-carbamide or carbonyl-dibenzamide, $CN^2H^2(C^7H^5O)^2$, identical with that which E. Schmidt obtained from benzamide and liquid phosgene (2nd Suppl. 263). It crystallises from alcohol in splendid needles, melts at 210° , and is resolved by prolonged

boiling with hydrochloric acid into benzoic acid and ammonia (D. McCreath, *Deut. Chem. Ges. Ber.* vii. 1739).

Guanidine carbonate fused with *urea* is converted into dicyano-diamidine, $C^2H^2N^4O$ (p. 600).

When guanidine hydrochloride is heated with *sarcosine*, or, when its alcoholic solution is boiled with *sarcosine*, the two bodies unite directly, forming a compound which dissolves easily in alcohol, and separates therefrom in fine tabular crystals. It is, however, somewhat unstable, being easily resolved into its components under the influence of platonic chloride, mercuric oxide, &c. (E. Baumann, *Deut. Chem. Ges. Ber.* vii. 1151).

A periodide of guanidine, $CH^3N^3.HI.I^2$, crystallising in prisms having the colour of iodine, is obtained by the action of iodine dissolved in hydriodic acid on guanidine carbonate. The corresponding bromine-compound, $CH^3N^3.HBr.Br^2$, appears to be produced by the action of bromine (3 mols.) on guanidine carbonate (1 mol.) It forms large red prisms which readily lose bromine (Kamenski, *ibid.* xi. 619).

SUBSTITUTED GUANIDINES.

Bromoguanidine, CH^3BrN^3 , is obtained by acting on guanidine carbonate (1 mol.) with bromine (1 mol.) and treating the product with water. It crystallises in small yellow needles, very slightly soluble in water and in ether, easily soluble in alcohol. Heated in a capillary tube it detonates at a few degrees above 100° (Kamenski, *loc. cit.*)

Chloroguanidine, CH^3ClN^3 , prepared in like manner, crystallises in the same form as the bromine-compound, but is lighter in colour and more stable than the latter, not detonating till it is heated to 147° .

Nitrosoguanidine, $CH^3(NO)N^3$, is obtained by dissolving nitrate of guanidine in excess of nitrous and fuming nitric acid. After the solution has stood for twenty-four hours, it is poured into an excess of cold water, whereupon the nitrosoguanidine is precipitated in colourless, flexible, needle-shaped crystals, soluble in hot water and in boiling alcohol, insoluble in ether and chloroform. Submitted to a gradually increasing temperature, nitrosoguanidine loses ammonia at 220° , the crystals becoming opaque without change of form. At higher temperatures cyanogen-compounds are given off, and a stable yellow substance remains, which is probably hydromellone (Jousselyn, *Compt. rend.* lxxxv. 548).

Methyl-guanidine, $CH^4(CH^3)N^3$, is formed by the action of cyanamide on methylamine hydrochloride, or of methyl-cyanamide on ammonium chloride (2nd *Suppl.* 582).

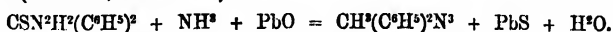
Ethyl-guanidine, $CH^4(C^2H^5)N^3$. The hydriodide of this base, obtained by the action of iodine on an alcoholic solution of thiocarbamide, crystallises from water in small needles which melt and decompose at 149° . The *sulphate* contains $1\frac{1}{2}$ mol. water, is easily soluble in water, sparingly in alcohol; melts and decomposes at 169° (A. Letnii, *Deut. Chem. Ges. Ber.* viii. 767).

Phenyl-, Toly-, and Xylyl-guanidines.

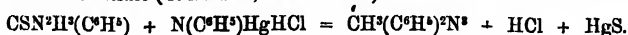
Diphenyl-guanidine, $C^{12}H^{12}N^3 = CH^3(C^6H^5)^2N^3$. *Melaniline*.

Formation.—1. By the action of cyanogen chloride or bromide on anhydrous aniline. This is the process by which melaniline was first prepared by Hofmann (iv. 461). According to Weith a. Ebert (*Deut. Chem. Ges. Ber.* viii. 912), diphenyl-guanidine (m. p. 147°) is produced by passing gaseous cyanogen chloride through cooled aniline; but if the aniline be heated to its boiling point, the product consists of tetraphenylmelamine, $C^8H^8(C^6H^5)^4N^6$ (m. p. 217°).

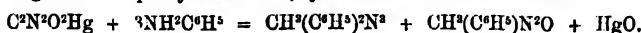
2. By the action of lead oxide on a solution of diphenyl-thiocarbamide in alcoholic ammonia (Hofmann, *Ber.* ii. 452):



3. By boiling an alcoholic solution of phenyl-thiocarbamide with mercuri-phenyl-ammonium chloride (precipitated on mixing the boiling solutions of aniline and mercuric chloride) as long as mercuric sulphide continues to be formed, and evaporating the alcoholic filtrate (C. Forster, *Ber.* vii. 294):

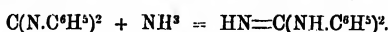


4. Together with phenyl-carbamide, by the action of aniline on mercuric fulminate,

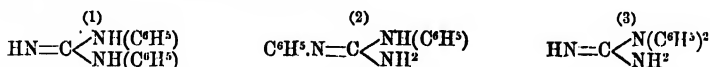


Dry mercuric fulminate is violently attacked by aniline, the mass being thrown out of the vessel and sometimes taking fire; but the action may be moderated by working with 100 grams of the fulminate, not dried but freed from the greater part of its moisture by pressure, and 100 grams of aniline (1 mol. fulminate to 3 mols. aniline) diluted with an equal volume of alcohol. The mixture becomes hot in about half-an-hour, and must then be cooled by placing the vessel in cold water, and frequently stirred. The product, consisting of mercury and a mass very much like amorphous phosphorus, is repeatedly exhausted with warm water containing hydrochloric acid; and the filtered solution, which contains phenyl-carbamide and a mercury-compound of diphenyl-guanidino, is treated with ammonia to decompose the latter and precipitate the mercury; then acidulated with hydrochloric acid, and evaporated to the crystallising point. Phenyl-carbamide then separates in needles (m. p. 149°), and the mother-liquors contain diphenyl-guanidino (m. p. 148°) (A. Steiner, *Ber.* vii. 1244; viii. 518).

5. By combination of ammonia with carbodiphenylimide (Weith, *Ber.* vii. 10);

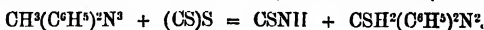


Constitution and Reactions.—Diphenyl-guanidino is susceptible of three modifications, represented by the following formulæ:



Only one of these is however actually known. The diphenyl-guanidino (melaniline) which Hofmann obtained by the action of cyanogen chloride on aniline was found by him to melt at about 130°, whereas that which he afterwards obtained by the action of lead oxide on a solution of diphenyl-thiocarbamide in alcoholic ammonia melted at 147°. These two bases were, therefore, regarded by Hofmann as isomeric, the latter being designated as α -, the former as β -diphenyl-guanidino.

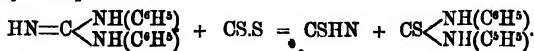
It has, however, been shown by Weith & Schroeder (*Ber.* vii. 937), that the diphenyl-guanidines obtained by the two processes above mentioned are identical in every respect, both melting at 147°, and exhibiting equal degrees of solubility in water and in alcohol; moreover they both react in the same manner with carbon disulphide, yielding thiocyanic acid and diphenyl-thiocarbamide (thiocarbamilide):



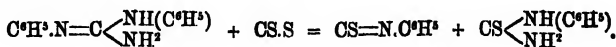
Two bye-products are also formed in this reaction, viz. a small quantity of phenyl-thiocarbimide, $CS=N-C^6H^5$, and a sulphuretted compound, not further examined, which crystallises in colourless needles melting at 152°–153°.

These results are corroborated by Hofmann in a more recent communication (*Ber.* vii. 947), in which he states that the so-called β -diphenyl-guanidino, or melaniline, obtained by the action of cyanogen chloride on aniline, has the same melting point as that prepared from diphenyl-thiocarbamide, viz. 147°. He still, however, thinks it not impossible that, under certain conditions, an isomeric diphenyl-guanidino may be produced from cyanogen chloride and aniline: since a small quantity of melaniline prepared in that way some years ago was found to retain the lower melting point (131°) which it originally exhibited, even after recrystallisation from alcohol, and after conversion into platinum salt and reconversion into the base.

Of the three possible formulæ for diphenyl-guanidino above given, the third is the least probable as a representative of the base actually known, since none of the decomposition-products of this body containing more than one atom of nitrogen appear to contain two phenyl-groups attached to the same nitrogen-atom. Further evidence against this formula is afforded by the fact that no diphenylamine is produced by heating diphenyl-guanidino prepared in either way, with hydrochloric acid. The reaction of diphenyl-guanidino with carbon disulphide affords an argument in favour of the first, or symmetrical formula of the base, as it takes place in the manner represented by the equation:



If diphenyl-guanidino had the constitution represented by the second formula, the reaction with carbon disulphide should yield phenyl-thiocarbimide and monophenyl-thiocarbamide: thus



As, however, a small quantity of phenyl-thiocarbimide was actually found among the

products, it is possible that the symmetrical diphenyl-guanidine may have been accompanied by a small amount of the second modification.

Diphenyl-guanidine heated for several hours to 170°–180° gives off ammonia and aniline, and leaves a resinous cake consisting of tetraphenyl-melamine (Hufmann, *Ber.* vii. 1736):



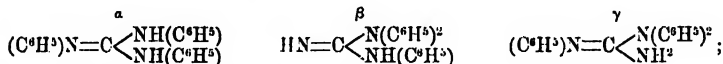
Diphenyl-guanidine heated with *acetic anhydride* to 100° yields monophenyl-acetyl-carbamide, $\text{CH}^3(\text{C}^6\text{H}^5)(\text{C}^2\text{H}^3\text{O})\text{N}^2\text{O}$, in needles melting at 183°. If the heat be raised to 150°, carbon dioxide is evolved and acetyl-diphenyl-carbamide, $\text{CH}(\text{C}^6\text{H}^5)^2(\text{C}^2\text{H}^3\text{O})\text{N}^2\text{O}$, is obtained, crystallising in needles which melt at 115° (D. McCreath, *Ber.* viii. 1181).

Dinitro-diphenyl-guanidine, $\text{C}^{13}\text{H}^{11}(\text{NO}^2)^2\text{N}^3$, is produced by desulphuration of dinitro-thiocarbaniide with lead oxide in presence of ammonia; it may be extracted from the resinous product by hydrochloric acid. It is nearly insoluble in water, but dissolves in alcohol and in ether, and crystallises from alcohol in small yellow shining laminae melting at 190° (Brückner, *Ber.* vii. 1234).

Ethyl-diphenyl-guanidine, $\text{C}^6\text{H}^5\text{N}=\text{C}<\begin{smallmatrix} \text{NH.C}^2\text{H}^5 \\ \text{NH.C}^2\text{H}^5 \end{smallmatrix}$, is formed (often together with α -triphenyl-guanidine), by addition of aniline to carbethyl-phenylimide, $\text{C}<\begin{smallmatrix} \text{N.C}^2\text{H}^5 \\ \text{N.C}^2\text{H}^5 \end{smallmatrix}$ (obtained by desulphurising a solution of ethyl-phenyl-thiocarbamide in boiling benzene with pulverised lead oxide). It forms a hydrochloride crystallising in needles, and a yellow platinohloride. It is decomposed by potassium hydroxide into carbon dioxide, aniline, and ethylamino (Weith, *Ber.* viii. 1530).

Dibenzoyl-diphenyl-guanidine, $\text{CH}(\text{C}^6\text{H}^5)^2(\text{C}^7\text{H}^5\text{O})^2\text{N}^3$, obtained by heating benzoic anhydride (1 mol.) and diphenyl-guanidine (1 mol.) to 100°, forms monoclinic crystals melting at 102° (McCreath, *ibid.* 383).

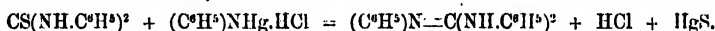
Triphenyl-guanidine, $\text{C}^6\text{H}^{11}\text{N}^3=\text{CH}^3(\text{C}^6\text{H}^5)^3\text{N}^3$. This compound admits of the three following modifications:



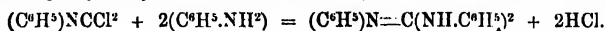
but only the first two are at present known.

The α -modification is produced by the following reactions:

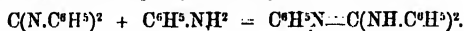
1. By the action of mercuri-phenyl-ammonium chloride on diphenyl-thiocarbamide (C. Forster, *Ber.* vii. 204):



2. From phenyl-isocyanochloride and aniline (Sell a. Zierold, *Ber.* vii. 1228):

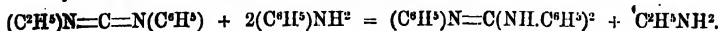


3. From aniline and carbodiphenylimide, by direct combination:



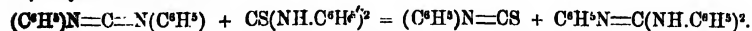
The hydrochloride of carbodiphenylimide may be used in the reaction; also the polymeric modification (m. p. 168°–170°), (Weith, *Ber.* vii. 10).

4. By the action of aniline on carbethyl-phenylimide:



The chief product of this reaction, however, is ethyl-diphenyl-guanidine, as already explained (*supra*).

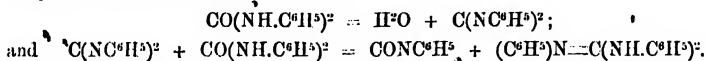
5. Together with phenyl-thiocarbimide, by heating carbodiphenylimide with diphenyl-thiocarbamide:



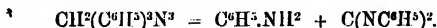
The action takes place at 100°, but becomes more energetic at 150°, and is still more quickly completed when a solution of carbodiphenylimide (1 mol.) in benzene is mixed with diphenyl-thiocarbamide (1 mol.) and hydrochloric acid (1 mol.) or hydriodic acid dissolved in alcohol, and the mixture is heated for a few minutes on the water-bath (p. 402), (Weith, *Ber.* ix. 810).

6. Small quantities of α -triphenyl-guanidine and benzonitril are produced, together

with phenyl isocyanate, by heating diphenyl-carbamide for four or five hours with phosphorus trichloride. The action appears to consist in the abstraction of water from the diphenyl-carbamide, and production of carbodiphenylimide, which latter acts upon another portion of the diphenyl-carbamide, producing phenyl isocyanate and α -triphenyl-guanidine (Weith, *loc. cit.*):



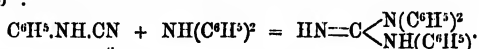
α -Triphenyl-guanidine crystallises from hot water, on cooling, in white needles melting at 143° (1st *Suppl.* 656). It begins to boil below 200° , and is decomposed by distillation, aniline passing over at first, mixed afterwards with α -triphenyl-guanidine, whilst the last portions of the distillate consist of almost pure carbodiphenylimide (m. p. 330° – 331° corr.) The decomposition of α -triphenyl-guanidine is therefore represented by the equation



The carbodiphenylimide and aniline, however, recombine as the temperature of the distillate becomes lower, reproducing the triphenyl-guanidine, so that the process is one of dissociation, like that which takes place in sal-ammoniac when heated (Weith, *Ber.* vii. 1303).

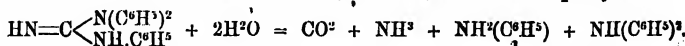
The hydrochloride of α -triphenyl-guanidine melts at 241° – 242° , and sublimes at a lower temperature in white slender needles (Weith, *Ber.* vii. 810). The hydrochloride of the triphenyl-guanidine which Sell a. Zierold obtained (p. 906) by the action of phenyl-isocyanochloride on aniline, is described as crystallising from aqueous alcohol in small white laminae melting at 207° . This would seem to show that the base of this salt is another modification of triphenyl-guanidine, and so in fact it is regarded by Sell a. Zierold; but its constitution, as indicated by its mode of formation, is clearly that of α -triphenyl-guanidine: hence there must either be an error in the determination of the melting point of the hydrochloride, or else the base, at the moment of its formation, must have undergone an atomic transposition.

β -Triphenyl-guanidine, $\text{HN}=\text{C} \begin{smallmatrix} \text{N}(\text{C}^6\text{H}_5)^2 \\ \text{NH}(\text{C}^6\text{H}_5) \end{smallmatrix}$, is formed by heating cyanilido (iv. 441) with diphenylamine hydrochloride, the heat being gradually raised during two hours to 125° :

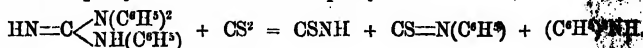


It crystallises in large, colourless, strongly refracting, isometric tablets, nearly insoluble in water, easily soluble in alcohol and ether, less easily in benzene and ligroin; melting at 131° . The hydrochloride crystallises with 1 mol. water in colourless thick tablets or prisms; 100 parts of water at 23° dissolve 28.4 parts of this salt. The *platinochloride* is at first a light yellow flocculent precipitate, which afterwards becomes darker and crystalline.

The colourless solution of the base in strong sulphuric acid acquires a splendid violet colour when heated. In a solution containing $\frac{500}{500}$ per cent. of the base, *chlorine-water* produces a distinct deposition of white flocks. The base heated to 260° with concentrated *hydrochloric acid* or *potassium hydroxide*, is resolved, after assumption of the elements of water, into carbon dioxide, ammonia, aniline, and diphenylamine:



When the base is heated to 150° – 160° for several hours with *carbon disulphide*, hydrogen sulphide is given off, and β -triphenyl-guanidine thiocyanato is produced, together with phenyl-thiocarbimide and diphenylamine:



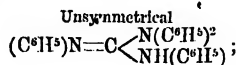
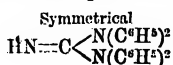
(Weith a. Schröder, *Ber.* viii. 912).

Trichlorophenyl-guanidine, $\text{CH}_2(\text{C}^6\text{H}_4\text{Cl})^3\text{N}^3$, is produced, together with chlorophenyl-thiocarbimide, $(\text{C}^6\text{H}_4\text{Cl})\text{NCS}$, chloraniline, chlorophenyl-carbamide, and a sulphur-compound crystallising in needles melting at 102° – 103° , by the action of iodine on an alcoholic solution of chlorophenyl-thiocarbamide, $\text{CS}(\text{NH}.\text{C}^6\text{H}_4\text{Cl})$. It crystallises from solution in carbon disulphide, in large crystals easily soluble in alcohol and ether, melting at 115° – 120° (Beilstein a. Kurlatow, *Ber.* vii. 730).

Diacetyl-triphenyl-guanidine, $\text{C}(\text{C}^2\text{H}_3\text{O})(\text{C}^6\text{H}_5)^3\text{N}^3$, is prepared by heating triphenyl-guanidine [?] a and acetic anhydride in molecular proportions to 100° for several hours; and *dibenzoyl-triphenyl-guanidine*, $\text{C}(\text{C}^7\text{H}_5\text{O})(\text{C}^6\text{H}_5)^3\text{N}^3$, in like manner.

with benzoic anhydride. Both crystallise in laminae; the acetyl-derivative melting at 131° , the benzoyl-derivative at 185° (McCreath, *Ber.* viii. 383).

Tetraphenyl-guanidine, $\text{CH}(\text{C}^6\text{H}_5)_3\text{N}^3$ (Weith, *Ber.* vii. 843). Of this compound there are two possible modifications, viz.:



but only the first is actually known.

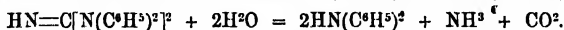
Tetraphenyl-guanidine is produced, together with a polymeric diphenyl-cyanamide, $n[\text{CN.N}(\text{C}^6\text{H}_5)_2]$, by the action of gaseous cyanogen chloride on fused diphenylamine. If a very strong heat be applied, the product consists mainly of the polymeric diphenyl-cyanamid $\bar{\epsilon}$. To prepare tetraphenyl-guanidine, diphenylamine is heated in an oil-bath to 150° – 170° , and a stream of pure cyanogen chloride is passed into it for a few hours. The product is dissolved in alcohol, and the solution, acidulated with hydrochloric acid, is poured into a large quantity of water, whereby unaltered diphenylamine is removed and the hydrochloride of tetraphenyl-guanidine produced; the filtrate is evaporated to a small bulk, and the oily layer of hydrochloride which separates and crystallises on cooling is decomposed by soda and recrystallised from ligroin.

Tetraphenyl-guanidine is insoluble in water, easily soluble in alcohol, ether, and benzene, and forms pyramidal crystals, sometimes modified, according to Kenngott, by longitudinal and transverse faces. It melts at 130° – 131° .

The salts of tetraphenyl-guanidine are for the most part sparingly soluble in water, and all crystallise well. The *hydrochloride* is easily soluble and crystallises in tablets (probably rhombic) containing $5\text{H}_2\text{O}$, and efflorescing on exposure to the air. Its solution is neutral, and gives with ferric chloride a rusty-brown precipitate which, after some time, changes into large yellow hexagonal plates of an *iron double salt*. The *platinochloride* is obtained as a light yellow precipitate which dissolves in boiling alcohol, and crystallises therefrom in shining laminae. The *nitrate* crystallises from boiling water in tufts of long needles having a satiny lustre. The *sulphate* forms slender needles very slightly soluble in water. The *hydriodide* crystallises from hot water in long colourless needles. The *chlorate* is a precipitate composed of slender needles, and so sparingly soluble that it is thrown down by potassium chlorate from 1 per cent. solutions of guanidine salts. Strong sulphuric acid, even in the cold, colours it a fine brick-red, changing first to violet and then to blue.

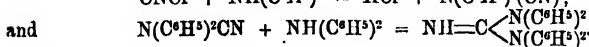
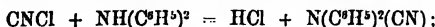
Potassium chromate produces in solutions of tetraphenyl-guanidine salts, a light yellow amorphous precipitate. *Chlorine-water* and *chloride of lime* produce in the solution of the hydrochloride, thick white precipitates. Strong *sulphuric acid* dissolves the pure base without colour at ordinary temperatures, but the solution, when heated, becomes violet red. *Carbon disulphide* does not act upon the base even at 180° .

Action of Potash.—When the hydrochloride of tetraphenyl-guanidine is heated to 200° with solid potash, it is decomposed, giving off ammonia and diphenylamine; and when the salt is heated with hydrochloric acid in sealed tubes to 330° – 340° , the same products are obtained, together with carbon dioxide, which in the former case unites with the potash. The reaction in both cases may be represented by the equation:



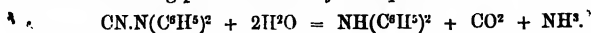
No aniline is produced in either case: hence the tetraphenyl-guanidine must have the constitution represented by the symmetrical formula above given; unsymmetrical tetraphenyl-guanidine would yield mono- as well as di-phenylamine.

The formation of tetraphenyl-guanidine by the action of cyanogen chloride on diphenylamine may be represented by the following equations:



The polymeric diphenyl-cyanamide, $n\text{C}_{13}\text{H}_{10}\text{N}_2 = n[\text{CN.N}(\text{C}^6\text{H}_5)_2]$, formed in large quantity, together with only a small quantity of tetraphenyl-guanidine, by the action of cyanogen chloride on diphenylamine at a very high temperature (250°), may easily be obtained pure and colourless, by crystallisation from alcohol. It differs essentially in its properties and reactions from the metameric compound, carbodiphenylimide, $(\text{C}^6\text{H}_5)_2\text{N}=\text{C}=\text{N}(\text{C}^6\text{H}_5)$ (p. 401). It crystallises in shining acute rhombohedrons, melts at 292° , is insoluble in water, and is dissolved only in traces by alcohol, ether, benzene, &c. It is somewhat soluble in hot oil of turpentine, and crystallises therefrom in colourless laminae. At a very high temperature it partly distils unaltered, and is partly resolved into benzonitril, carbon, &c. Heated with strong sulphuric acid, it dissolves with splendid violet colour (the reaction exhibited

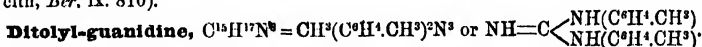
by the sulpho-acids of diphenylamine). Heated to 250° in sealed tubes with hydrochloric acid, it is resolved into carbon dioxide, ammonia, and diphenylamine; and the same result is obtained by heating it very strongly with potassium hydroxide. Hence it follows that in each of the groups forming the polymeric diphenyl-cyanamide, the two phenyl-groups must be attached to the same atom of nitrogen, the reactions above-mentioned taking place as shown by the equation:



Carbodiphenylimide, on the other hand, which has only one phenyl-group attached to each nitrogen atom, yields by similar treatment nothing but carbon dioxide and aniline.

That the diphenyl-cyanamide obtained by the action of cyanogen chloride on diphenylamine, is really a polymeric, and, according to all analogy, $(\text{C}_6\text{H}_5)_2\text{N}_2$, that is to say, porphenyl-melamine, is shown by its behaviour with aniline and diphenylamine, on which it does not exert the slightest action, whereas the simple diphenyl-cyanamide, $\text{C}_6\text{H}_5\text{N}_2$, would form tri- and tetraphenyl-guanidine respectively. The polymeric diphenyl-cyanamide is not converted into the simple cyanamide by distillation. Dehydrated tetraphenyl-guanidine hydrochloride, heated to 280° - 300° in sealed tubes for four or five hours, is resolved into diphenylamine hydrochloride and the polymeric diphenyl-cyanamide: hence the occurrence of the latter in the preparation of tetraphenyl-guanidine.

Phenyl-tolyl-guanidine, $\text{CH}_3(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4.\text{CH}_3)\text{N}_2$. The hydrochloride of this base is formed, together with small quantities of phenyl-thiocarbimide and paratolyl-thiocarbimide, when a mixture of diparatolyl-thiocarbamide, hydrochloric acid, and carbodiphenylimide is heated with alcohol to the boiling point for about an hour. (Weith, *Ber.* ix. 810).



Metoluidine.—This base, homologous with diphenyl-guanidine or melaniline, was first obtained by W. Wilson (*Chem. Soc. Jour.* 1850, 154), who prepared it by passing cyanogen chloride over toluidine spread in a thin layer over the surface of a bent glass tube. The product thus obtained is a resinous mass consisting almost entirely of the hydrochloride of ditolyl-guanidine, from which the base may be obtained by dissolving the mass in very dilute hydrochloric acid, and precipitating the filtrate with potash. For purification, the precipitate is boiled for some time to expel unaltered toluidine, then washed, and crystallised from aqueous alcohol. It is also produced, similarly to diphenyl-guanidine (p. 904), by desulphuration of ditolyl-thiocarbamide in presence of ammonia (Hofmann, *Ber.* vii. 1736). It is sparingly soluble in cold, more easily in hot water, and crystallises in laminae (Wilson); in slender needles melting at 168° (Hofmann). When heated, it behaves like diphenyl-guanidine, giving off ammonia, and leaving tetratolyl-melamine, in the form of a resinous mass which slowly acquires a crystalline structure and forms a hydrochloride crystallising in concentric groups of slender needles.

Tritolyl-guanidine, $\text{C}_6\text{H}_5\text{N}_2 = \text{CH}_3(\text{C}_6\text{H}_7)_2\text{N}_2$, is formed by heating monoparatolyl-carbamide with paratoluidine and phosphorus trichloride (Weith, *Ber.* ix. 820).

Dixyl-guanidine, $\text{C}_6\text{H}_5\text{N}_2 = \text{CH}_3(\text{C}_6\text{H}_9)_2\text{N}_2$, is readily formed by desulphurising dixyl-thiocarbamide with lead oxide in presence of alcoholic ammonia. It crystallises in white slender needles, quite insoluble in water, and melting at 156° - 158° . Its salts crystallise remarkably well (Hofmann, *Ber.* ix. 1292).

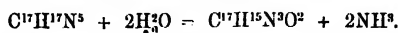
A *trixyl-guanidine*, $\text{CH}_3(\text{C}_6\text{H}_9)_3\text{N}_2$, is formed by desulphurising an alcoholic solution of xylyl-thiocarbamide with lead oxide in presence of xylylidine (Hofmann).

Cyanoguanidines and Oxalylguanidines (Landgrebe, *Ber.* x. 1587).

Dicyanodiphenyl-guanidine, $\text{C}_6\text{H}_5\text{N}_3$, is identical with dicyanmelaniline, the compound which Hofmann obtained by passing cyanogen gas into a saturated solution of melaniline (diphenyl-guanidine) in cold alcohol (*iv.* 465).

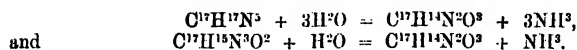
Dicyanoditolyl-guanidine, $\text{C}_6\text{H}_5\text{N}_3$, is formed in like manner by passing cyanogen into an ethereal solution of ditolyl-guanidine, the liquid solidifying to a pulp of long needles. It is sparingly soluble in water, more easily in ether and in alcohol; the alcoholic solution turns brown and decomposes at about 50° . From ether the base separates in well-defined limpid prisms, which begin to decompose at 70° - 80° , and are converted into a brown resin at 150° . The alcoholic solution forms white precipitates with *silver nitrate* and *mercuric chloride*. With *acids*, dicyanoditolyl-guanidine reacts exactly like the corresponding phenyl-compound,

Ditolyloxalyl-guanidine or **Cyanditolyloxamide**, $C^{17}H^{15}N^3O^2$, homologous with melanoximide or cyanodiphenyl-oxamide (iv. 286), is formed, like the latter, by the action of dilute acids on dicyanoditoly-guanidine:



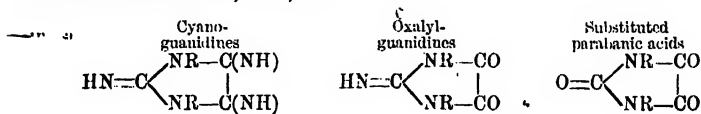
It is insoluble in water, slightly soluble in cold alcohol and ether; crystallises from hot alcohol in colourless needles often grouped in rosettes; melts at 188.5° . By acids and alkalis it is resolved into oxalic acid and ditolyl-guanidine. Heated with aniline, it forms, with evolution of ammonia, a base, $C^{22}H^{19}N^3O^2$, the hydrochloride of which crystallises from alcohol in small needles.

Ditolyloxalyl-guanidine and dicyanoditoly-guanidine, treated in boiling alcoholic solution with a dilute acid, are converted into ditolyl-parabanic acid, $C^{17}H^{14}N^2O^3$, homologous with diphenyl-parabanic acid (iv. 340):

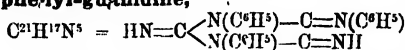


Ditolyl-parabanic acid is most easily produced from the oxalyl-compound, but resinous products are always formed at the same time. It crystallises in nacreous laminæ melting at 144° , easily soluble in benzene and in alcohol, sparingly in ether, carbon disulphide, and glacial acetic acid. With acids and alkalis it reacts like diphenyl-parabanic acid (iv. 340).

The compounds just described may be represented by the following formulæ, in which R stands for C^6H^5 , C^7H^7 , &c.



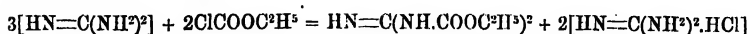
β -Dicyanotriphenyl-guanidine,



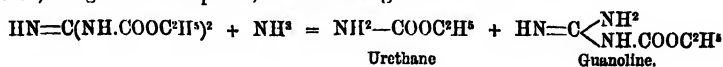
The hydrochloride of this base, $C^{21}H^{17}N^3.HCl + 3H^2O$, is obtained by heating the mixed solutions of dicyanodiphenyl-guanidine and aniline hydrochloride, then adding water, and crystallising the resulting precipitate several times from hot alcohol. It forms yellow-brown needles, which give off their water and turn red at 140° , and decompose at 250° . The free base, $C^{21}H^{17}N.1\frac{1}{2}H^2O$, may be prepared by dissolving the hydrochloride in hot alcohol containing ammonia, heating the liquid for some time, and adding water; it then separates as an amorphous precipitate which soon becomes crystalline. By repeated crystallisation from alcohol it is obtained in dark brown needles with violet iridescence, which give off their water of crystallisation at 120° , and melt at 172.5° . It is insoluble in water, but dissolves in alcohol, ether, and carbon disulphide. Its salts crystallise well, the *platinochloride* in yellow needles, easily soluble in alcohol.

The base appears to be identical with that which Hofmann obtained, together with cyananiline, by the action of cyanogen on aniline, and isomeric with that which he prepared by the action of cyanogen on α -triphenyl-guanidine (2nd Suppl. 583).

GUANIDOCARBONIC ETHERS (Noncki, *Ber.* vii. 1588; *J. pr. Chem.* [2], xvii. 237). *Diethylic Guanidocarbonate*, $C^4H^{12}N^3O^4$, or $\text{HN}=\text{C}(\text{NH.COOC}^2\text{H}^5)^2$, is prepared by gradually adding ethylic chlorocarbonate to a concentrated alcoholic solution of guanidine contained in a small flask which is kept cool. The ether then separates in needle-shaped crystals, and the alcoholic mother-liquor contains guanidine hydrochloride:



Diethylic guanidocarbonate is insoluble in water, but dissolves easily in absolute alcohol and ether, with moderate facility also in dilute alcohol, and is best crystallised therefrom. It melts at 162° . Dilute sulphuric and hydrochloric acid decompose it readily. Heated to 400° in a sealed tube with alcoholic ammonia, it is converted into urethane and ethylic guanidomonocarbonate, $C^4N^2H^8O^2$, which, being a basic compound, is also called *guanoline*:



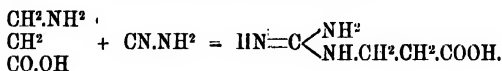
Two molecules of guanoline contain the elements of 1 mol. guanidine and 1 mol. diethylic guanidodicarbonate :



The formation of guanoline was once observed on adding an aqueous solution of guanidine (containing a little ammonia) to ethylic chlorocarbonate.

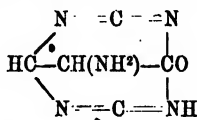
Guanoline crystallises from aqueous or alcoholic solution in rhombic laminae containing $\text{C}^4\text{H}^8\text{N}^3\text{O}^2 \cdot \text{H}^2\text{O}$. The hydrated base melts at 100° ; the anhydrous base at 114° – 115° . The *nitrate*, $\text{C}^4\text{H}^8\text{N}^3\text{O}^2 \cdot \text{NO}^3\text{H}$, crystallises in fine rhombic prisms; the *neutral sulphate* has the composition $(\text{C}^4\text{H}^8\text{N}^3\text{O}^2)^2\text{SO}^4\text{H}^2$; the *platinochloride* is $(\text{C}^4\text{H}^8\text{N}^3\text{O}^2)^2 \cdot 2\text{HCl} \cdot \text{PtCl}_4$.

β. Guanidopropionic acid, $\text{C}^4\text{H}^8\text{N}^3\text{O}^2 = \text{HN}=\text{C} \begin{smallmatrix} \text{NH}^2 \\ \text{NH} \cdot \text{CH}^2 \cdot \text{CH}^2 \cdot \text{CO} \cdot \text{OH} \end{smallmatrix}$ metameric with guanoline and with creatine, is formed on adding ammonia to a solution of *β*-amidopropionic acid (2 pts.) and cyanamide (0·7 pt.):



It is a very stable compound, not decomposing till heated to 205° – 210° (E. Mulder, *Ber.* viii. 1261; ix. 1902).

GUANINE, $\text{C}^4\text{H}^6\text{N}^4\text{O}$. This base has the composition of amidosarcine, $\text{C}^4\text{H}^6(\text{N}^2\text{H}^2)\text{N}^2\text{O}$, and may be represented by the constitutional formula :



(Grimaux, *Ann. Ch. Phys.* [5], xi. 356); see URIC ACID.

Guanine has been found: (1). Together with other bases in the extract obtained by boiling yeast with water (p. 783). (2). To the amount of 5 to 8 per cent. together with sarcine, in the sperm of the salmon (Piccard, *Ber.* vii. 1714). (3). In small quantity in the urine of a pig, which was fed exclusively on bran, and appeared to be suffering from gout (Pecile, *Liebig's Annalen*, clxxxiii. 141).

GUANO. The following analyses of Peruvian guanos, from as yet unworked deposits, taken during the survey of H.M.S. *Petrel*, have been made by Voelcker (*Journ. Roy. Agr. Soc.* 1874, 541).

	Guano from Pabillon de Pica				
	La Barlo- venta : white guano from surface	La Cueva, 25 feet from surface	San Lo- renzo, 15 ft. from surface	Cueva del Rinconada	
				Surface	50 ft. from surface
Moisture	4·13	3·20	5·45	9·23	6·70
Organic matter and ammonium salts }	59·01	46·17	49·40	41·32	55·10
Earthy phosphates . .	21·82	25·51	27·01	23·80	24·55
Alkali salts	9·00	15·49	15·99	23·30	12·10
Sand	6·04	9·63	2·15	2·35	1·55
Phosphoric acid . . .	11·67	13·49	14·06	11·57	14·72
Total Nitrogen . . .	15·08	9·81	9·15	6·68	11·02
Nitric acid	·04	·01	·61	·90	1·20

PERUVIAN GUANOS.

	Huacillos guano.					Punta de Lobos guano		
	5 ft. from surface	10 ft. from surface	13 ft. from surface	19 ft. from surface	40 ft. from surface	5 ft. from surface	8 ft. from surface	40 ft. from surface
Moisture	8.23	5.25	15.39	12.67	8.66	14.53	4.79	14.06
Organic matter and ammonium salts }	46.46	41.90	34.21	34.83	47.09	35.77	17.14	49.74
Earthy phosphates . .	22.45	30.21	24.71	33.20	24.20	26.50	23.09	21.40
Alkali salts	19.22	16.73	23.09	15.69	16.65	20.35	27.04	13.45
Sand	3.64	5.91	2.60	3.61	3.40	2.85	27.94	1.35
Phosphoric acid . . .	15.62	15.30	12.93	16.65	14.35	15.34	10.95	11.01
Total nitrogen . . .	10.40	7.45	6.65	6.72	8.81	6.55	2.64	9.99
Nitric acid	2.87	2.16	.25	.35	1.10	3.40	.29	3.50

The total amount of these deposits is about 7,301,000 tons, to which the deposits at Papillon de Pica contribute 5,000,000. With one exception, the guanos are not equal to the old Chincha guano, which contained 14 per cent. of nitrogen, but they are mostly in excellent condition, dry, and free from lumps. Guano does not seem to alter steadily in composition with the depth from surface, its composition apparently depending less on its age than on other circumstances. The nitric acid of the Peruvian nitre beds may possibly be derived from ancient guano.

Phosphatic guanos (Voelker, *Journ. Roy. Ag. Soc.* [2], xii. 440-459). Angamos guano, from the Bolivian coast, affords the best example of the rapidly dried recent excrement of sea-birds; this guano is acid to litmus, and contains 19-21 per cent. of nitrogen. Bird-dung, exposed to the weather in various climates, undergoes change, and guanos of various qualities are produced. The ultimate effect of rain is to destroy the organic matter; the guano then remaining is said to be 'phosphatic,' and contains very little nitrogen. These phosphatic guanos are of great value as materials for high-class superphosphate. The annexed table gives more or less complete analyses of a number of phosphatic guanos. In many instances, the bases present are insufficient to form tribasic salts with the phosphoric acid; this is especially the case in the stony masses, known as 'crust' guanos, frequently found in deposits much altered by weather. Mejillones guano is a deposit near the coast of Bolivia, estimated at several million tons; the phosphoric acid, on an average of 12 analyses, is equal to 72.1 per cent. tricalcic phosphate. Some of the guanos from islands in the Gulf of California contain over 80 per cent. of tricalcic phosphate. Curaçoa Island is on the coast of Venezuela; a rock-phosphate from Great Curaçoa yielded 81.9 per cent. tricalcic phosphate. The five guanos next mentioned in the table are of little importance. Baker, Howland, and Jarvis Islands lie near the equator, in the Pacific Ocean; their guano is now nearly exhausted; the analysis of Jarvis Island guano represents the present inferior importations; calcium sulphate is often present. Shaw's, Malden, Enderbury, and Starbuck Islands are coral islands in the South Pacific Ocean; the guano is of high quality, but apt to be contaminated with fragments of the coral rock. The South American guanos are seen, from the analyses, to contain a large quantity of water and sand, and to be richer in nitrogen than the others mentioned; they vary much in composition. Patos Island is on the coast of Lower California. Bird's Island belongs to the Pacific group.

PERCENTAGE COMPOSITION OF PHOSPHATIC GUANOS.

	Mejillones	Gulf of California		Curaçao Island.		Quito Herrero Island		Petrel Island		Coral Island		Booby Island		McKean Island		Baker Island		Howland Island		Jarvis Island		Shaw's Island		Pint Island		Malden Island		Enderbury Island		Starbuck Island	
		1	2	1	6	1	1	1	1	1	1	1	1	1	1	1	3	1	1	1	1	1	1	1	1	6	1	1	1	1	1
Water	7.68	4.83	11.07	8.50	9.51	7.04	6.10	12.55	12.05	11.42	11.27																				
Loss on ignition	6.38	12.72	7.11			11.76	10.18	9.59	6.25	6.38	9.93																				
Phosphoric acid*	33.46	34.33	31.64	32.44	30.50	35.29	21.77	22.68	32.32	34.12	23.88	34.69	37.13	33.85	28.74	37.79	33.61	45.57													
Lime	37.01	37.36	40.41	39.41	36.44	41.76	45.36	36.34	42.34	41.58	37.18	43.26	48.43	45.43	40.76	41.96	41.04	40.94													
Magnesia	3.13	1.76	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—													
Alkali salts	5.69	5.54	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—													
Sulphuric acid	3.28	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—													
Carbonic acid	.91	.46	2.64	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—													
Siliceous matter	1.86	1.69	.21	2.55	5.50	.60	.09	.79	.14	.22	.09	.85	.19	.10	.09	.06	.02	.07													
Nitrogen	.89	1.04	—	—	—	.38	—	.26	[.53]	—	—	—	—	—	—	—	—	—													
* Equal to tricalcic phosphate	73.04	74.94	69.01	70.82	66.58	77.05	47.52	49.56	70.55	74.48	52.13	75.73	81.05	73.89	62.74	82.49	73.67	99.48													

PERCENTAGE COMPOSITION OF PHOSPHATIC GUANOS.

	Falkland Islands		Patagonian		Fates Island	Bird's Island
Number of Analyses	1.	1.	1.	1.	1.	1.
Water	33.43	35.86	21.46*	6.59	14.35	6.92
Loss on ignition	21.42	26.07	11.74	10.23	10.24	4.80
Phosphate of calcium	32.04	22.01	27.61	23.44*	53.48	80.44
Carbonate of calcium	2.52	5.64	2.99	—	2.58	6.38
Sulphate of calcium	—	—	—	—	—	—
Alkali salts, &c.	6.22	7.34	6.07	9.05	4.63	1.34
Siliceous matter	4.37	3.08	30.13	50.69	14.72	.12
Nitrogen	4.3	4.42	1.83	.90	.96	—

Bats' Guano. By A. Voeleker (*Jour. Roy. Agri. Soc.* 1878, 60-72). This material is found in the caves inhabited by bats; large quantities have been discovered in Arkansas and Texas, and on the Bahama Islands; the deposits from the latter are known as Guanahani guano. Both texture and composition are very variable. Some specimens are light coloured, dry, and powdery, and full of the undigested wings of insects. Other specimens are dark, damp, and lumpy, and of an earthy texture. The guano has very little odour. The following table shows the principal ingredients of a new and old deposit* from caves in Arkansas, and the mean composition of eight cargoes imported from the Bahamas, with the highest and lowest percentages:—

	Arkansas Guano		Bahama Guano		
	Old deposit	New deposit	Highest percentages	Lowest percentages	Mean
Water	6.74	33.53	31.40	9.45	24.02
Organic matter	21.32	44.63	27.97	10.74	14.96
Ash	71.94	21.84	79.14	50.76	61.02
Nitrogen as organic matter and ammonia	2.48	6.62	1.93	0.53	0.89
Nitrogen as nitric acid	0.46	2.18	1.06	0.23	0.47
Total nitrogen	2.94	8.80	2.99	0.80	1.36
Phosphoric acid	6.64	3.76	21.09	4.59	13.49

As with most other guanos, the recent deposits are rich in nitrogen and poor in phosphates, while in the older and more decomposed deposits the proportion is reversed. Nitrates are present in all specimens. A small part of the phosphoric acid exists in the soluble form. The chief constituents of the ash, besides phosphates, are siliceous matter, and carbonate and sulphate of calcium, but the proportions are very variable. The composition of bats' guano from Spain, Jamaica, and Penang (the latter is known as 'Typelawer') was found to range nearly within the limits above given (see also p. 765).

FISH GUANO. A sample of Norwegian fish guano steamed and deprived of fat, supplied by the firm of Otto Raddo in Hamburg, has been analysed by H. Vohl (*Dingl. pol. J.* cxv. 461) with the following results:

P ² O ⁵	CaO	MgO	NaCl	KCl	Fe ² O ³	S and CO ²	SiO ²	H ² O	N	Organic substance	
13.894	16.431	0.468	1.392	trace	0.023	1.534	3.069	0.886	6.393	8.673	47.167
37.697 ash									62.308 volatile and organic matter		

This guano contains about 12 per cent. nitrogen, and gives up to cold water 33-34 per cent. of its weight, the solution containing, besides easily soluble phosphates, 15 per cent. nitrogen in the residue dried at 100°. It passes into putrefactive decom-

position at 11°, whereas fish guanos still containing fat are very slow in putrefying. Disintegration with sulphuric acid is not advantageous, as the sulphuric acid is chiefly taken up by the organic matter; even when it was added to the amount of 30 per cent. the product contained only 3·58 to 3·60 per cent. soluble phosphoric acid. Better results were obtained by treating the guano first with an alkali and then with sulphuric acid, but this mode of decomposition is for the most part too costly.

The decomposition of the insoluble nitrogen-compounds in fish-guano is sometimes effected by moistening with water or urine, and leaving the mass in ferment. For 50 kilos. of manure 30 litres of urine or water are necessary; 5 kilos. of gypsum are added, and the heaps are covered with gypsum or earth to prevent loss of nitrogen. The temperature rises to above 40°, and when it begins to fall, the fermentation is over (A. Paget, *Chem. Centr.* 1877, 206). It has, however, been found by several experiments that the best method of bringing the nitrogenous matter, and likewise the phosphoric acid, into the soluble state, is to feed cattle with the guano and use their excrements as manure. In the following experiments, fish-guano, mixed with groats, was given to two sheep, which ate it readily. The guano contained 56·04 per cent. albuminoids (9·44 nitrogen), 2·11 fat, and 41·85 mineral matter.

The following analyses show the composition of the dried excrements of the animals; A when each sheep was fed on 656·85 grams of dry hay and 400 grams of groats per day, and B when 150 grams of fish meal were added to the above rations:

	A		B	
	No. I.	No. II.	No. I.	No. II.
Albuminoids	10·42	9·75	10·94	10·81
Fibre	41·33	42·23	34·16	34·07
Fat	3·50	3·22	3·19	3·26
Non-nitrogenous extractive matter . .	34·10	33·96	31·19	31·64
Ash	10·95	10·84	20·52	20·22
Total weight of dry excrement per day	427·04	420·51	442·90	445·68

Water containing carbonic acid in solution, dissolved 18·35 per cent. of the phosphoric acid contained in the fish-guano, and 67·5 per cent. of the phosphoric acid in the fresh sheep dung. After the dung had been kept for two months, and decomposition had set in, the solubility of the phosphoric acid rose to 73·24 per cent. These results show that the value of the fish-guano as a manure is increased by passing through the alimentary canal of the animals (O. Kellner, *Landw. Versuchs-Stationen*, xx. 423).

The proportions of phosphoric acid, nitrogen, and ash in various guanos and other manures have been determined by P. Wagner (*Ber. d. Landw. Versuchs-St. Darmstadt*, 1874):

	Phosphoric acid	Nitrogen	Ash
Fish guano	11·6	8·1	41·2
Whale guano	11·4	6·5	44·1
Frey Bentos guano	15·70	6·21	41·02
Peru guano	10·7—15·9	3·3—14·3	—
„ (disintegrated)	8·7— 8·10	8·1—10·3	—
Bone-meal	18—19	3·4	—
Steamed bone-meal	20·26	3·25	—

On the Composition of Guano, see also Chevroul (*Compt. rend.* lxxvi. 1376, 1500; lxxvii. 155, 453, 569, 901; *Chem. Soc. Jour.* 1873, 1052; 1874, 90).

The name 'European guano' is applied to various mixtures of horn, blood, urine, dung, calcium phosphate, wool, vegetable albumin, &c., containing, on the average, 5·2 per cent. nitrogen, 6·2 soluble phosphoric acid, and 0·8 potash.

GUANOLINE, $C^4H^3N^3O^2$. See GUANIDO-CARBONIC ETHERS (p. 910).

GUANOVLITE (F. Wibel, *Ber.* vii. 322). A mineral, found by C. Gottsche, forming the interior of a crushed bird's egg from crude Peruvian guano, the shell of which consisted of calcium phosphate and carbonate, coloured brown by organic matter. It is yellowish-white, with a silky to satiny lustre and laminar structure. Hardness = 2. Sp. gr. = 2·33—2·65 at 15°. When heated it remains unaltered at 100°, but at 141° it gives off 10·91 per cent. consisting of water and ammonia with a little sal-ammoniac, and at 190° it blackens; the entire loss amounts to 36·10 per cent. Analysis showed that the mineral has the composition $(NH^4)^2SO^4 \cdot 2K^2SO^4 \cdot 3KHSO^4 \cdot 4H^2O$, with traces of ammonium chloride, lime, soda, phosphoric acid, organic matter, &c.

That it cannot be wholly derived from the constituents of the egg itself, is evident from the fact that some of the eggs are almost filled with it; the quantities of potash and sulphuric acid are much larger than would be contained in the fresh egg, and must, therefore, have been introduced by diffusion, whilst the soda, phosphoric acid, &c., were removed by the same process. The most remarkable feature is, however, the presence of the acid potassium sulphate, which has hitherto been known only in the rare volcanic mineral, misenite. On evaporating a solution of guanov. lite at ordinary temperatures, it separates out unchanged, in crystals belonging to the rhombic system, but the solution, when heated, becomes strongly acid, and deposits the three constituents separately.

¹ **GUARANA.** For the preparation of caffeine from this substance, the following method is recommended by F. V. Greene (*Pharm. J. Trans.* [3], vii. 87) in preference to that given by Stenhouse (i. 708). Powdered guarana is mixed with three times its weight of finely divided litharge, and boiled in distilled water until, on leaving it to cool, the insoluble portion rapidly subsides. The cool, clear liquid is then filtered, and the residue washed with boiling water, till the washings produce no precipitate with phosphomolybdic acid or platinum chloride. The small amount of lead in the filtrate is then precipitated by sulphuretted hydrogen, and the solution on evaporation yields colourless crystals of caffeine, which may be recrystallised from alcohol.

The tannin of guarana is found by Green (*ibid.* 328) to differ in several of its reactions from ordinary tannin, for which reason he regards it as a distinct compound, and proposes to call it *Paullitanic acid*.

GUAYACANITE. The variety of enargite from the Cordilleras of Chile, so named by Field (ii. 488), is regarded by Frenzel as identical with luzonite (see ENARGITE, p. 733).

GUM. It is commonly supposed that the formation of gum in plants is due to a transformation of the cell-wall, but from microscopic observations by E. Prillienx (*Compt. rend.* lxxviii. 155) it appears that gum is produced in the interior of the vessels in the form of small drops which gradually unite. According to Mercadante, on the other hand (*Bert. Ber.* ix. 581), gum and starch are formed simultaneously in the plant-cell, the gum on the walls, the starch in the interior. At a later stage, the gum increases in quantity while the starch diminishes; but this result is not due to a conversion of the starch into gum, the starch being, in fact, converted into the soluble modification, which serves for the nutrition of the plant.

According to Schützenborger, ordinary gum (arabin) is contained in considerable quantity in the extract obtained by boiling yeast with water (p. 783).

On the Gum of Sugar-beet and the so-called 'fermentation-gum,' obtained from Beet-juice which has passed into the state of mucous fermentation, see ARABIN (p. 118).

On Kauri or Cowdie gum, the produce of *Dammara australis*, see DAMMARA RESIN (p. 625).

Quebracho Gum.—The *Quebracho Colorado* (*Loxopterygium Lorentii*, Grisebach) is a tree belonging to the Anacardiaceous order, indigenous in, and peculiar to, the northern part of the Argentine Republic. The so-called gum, or rather thickened juice, collects in the cracks and hollows of the wood, in ruby-red concretions somewhat resembling colophony, but more brittle; it is easily pulverised, and yields a brick-red powder. It is scentless, but has a slightly astringent taste. Sp. gr. 1.3756 at 15°. It is easily soluble in alcohol, acetone, and acetic ether; dissolves also in amyl alcohol and acetic acid, but is insoluble in benzene, carbon bisulphide, chloroform, and turpentine oil; nearly insoluble in cold water and in ether; nevertheless an ethereal solution, having an emerald-green colour, may be obtained by agitating the gum with ether and water. Boiling water dissolves it completely, and deposits part of it on cooling. It dissolves also in strong sulphuric acid, and is precipitated therefrom by water. Heated in a platinum capsule it swells up and burns, leaving a shining porous cinder, which burns away slowly on continuing the heat. If the combustion be completed in a stream of oxygen, the unburnt residue is scarcely appreciable.

A 1 per cent. solution of the gum in absolute alcohol, in a layer 7 mm. thick, exhibits an absorption-spectrum having a dark band commencing between the solar lines A and B, and terminating at G; another extending for a short distance on each side of D; and a third beginning half-way between D and E and extending to all the more refrangible part of the spectrum. The same solution in a layer 25 mm. thick absorbs the whole of the spectrum, excepting a narrow space from C half-way to D. A solution of dragon's blood, which in some respects resembles quebracho gum, exhibits a very different spectrum, containing a dark band extending for a short distance on each side of C, and a second beginning just beyond D and occupying all the rest of the spectrum.

Reactions.—Quebracho gum, subjected to dry distillation, yields between 100° and 120° a distillate which remains liquid on cooling, and between 240° and 245° a distillate which solidifies to colourless prisms of pyrocatechin (m. p. 105° nearly, b. p. 240°–245°). The gum is strongly attacked by concentrated *nitric acid*, and when heated with the same acid somewhat diluted with water, it is oxidised to oxalic acid and trinitrophénol or picric acid. Fused with *potash* it yields proto-catechuic acid, $C^7H^4O^4$, or $C^6H^3(OH)^2.COOH$, and phloroglucin, $C^6H^4O^3$.

The formation of these products renders it probable that quebracho gum contains one of the bodies called catechins (see p. 415); but, in consequence of the great tendency of these bodies to alteration, their actual presence in the gum has not been satisfactorily demonstrated. The existence of catechin in an anacardiaceous plant would be a novelty, this body having hitherto been found only in the leguminosæ, rubiaceæ, and ædrnlaceæ orders (Pedro N. Arata, *Anales de la Sociedad Científica Argentina*, July 1878).

Sonora gum is a name given in Mexico to crude shellac (*q.v.*)

GUM-RESINS. See RESINS.

GUN-COTTON. From analyses made by reduction with ferrous salts, Champion a. Pellet (*Compt. rend.* lxxxiii. 707; lxxxiv. 609) conclude that Abel's compressed gun-cotton consists not of trinitrocellulose, as stated by Abel (*1st Suppl.* 659), but of pentanitrocellulose. Abel, on the other hand (*Compt. rend.* lxxxiii. 1011), shows that the analyses on which this conclusion is founded are defective, inasmuch as no care was taken to free the gun-cotton from admixed nitro-derivatives of fatty and resinous substances, by washing with alcohol and ether. Gun-cotton, prepared with the utmost care in his own laboratory, exhibited the composition of trinitrocellulose, as determined several years ago by Walter Crum and by Pelouze, whereas commercial gun-cotton was found to be a mixture of about 85 per cent. trinitrocellulose with about 4 or 5 per cent. of unattacked cellulose and 10 per cent. dinitrocellulose.

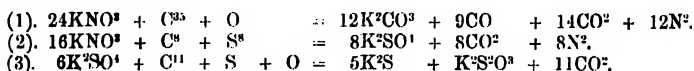
Böttger (*Diagl. pol. J. ex.* 315) finds that gun-cotton is dissolved by a boiling solution of *sodium stannite*, and that the regenerated cellulose is precipitated on adding to the liquid an excess of hydrochloric acid. As cellulose itself is not dissolved by sodium stannite, this reaction affords an easy method of determining the amount of unaltered cotton in a sample of gun-cotton.

On the Heat of Combustion of Gun-cotton, see EXPLOSION (p. 767).

On the Heat disengaged in its Formation, see HEAT.

On the Spectrum of Exploding Gun-cotton, see Lohse (*Pogg. Ann.* cl. 641; *Jahresb. f. Chem.* 1873, 151).

GUNPOWDER. *Decomposition.*—The following equations, representing different stages of the decomposition of gunpowder, are given by Debus (*Brit. Assoc. Reports*, 1875 [2], 40):



From the thermic effects produced by the explosion of gunpowder, Berthelot infers (*Compt. rend.* lxxxii. 475) that the explosion gives rise to the formation of all the compounds that are permanent under the circumstances of the experiment, chiefly sulphur, potassium carbonate, and potassium sulphate, together with carbon monoxide and dioxide, nitrogen, and vapour of water. The proportions of these several products vary with the local circumstances of the mixing and of the ignition. If the products remained in contact for a considerable time, their reciprocal actions would bring them into the condition which is consistent with the greatest possible evolution of heat,—that is to say, it would lead to their ultimate conversion into K^2SO^4 and CO^2 ; but the sudden cooling prevents the completion of this reaction. Nevertheless each of the products is formed in a regular manner, and the chemical transformation of powder may in all cases be represented by a system of very simple equations.

On the Heat of Combustion of Powder, see p. 767; also De Tromenee (*Compt. rend.* lxxvi. 384; *Jahresb. f. Chem.* [1873], 1026).

On a method of testing the Fineness of Gunpowder, depending on the intensity of its combustion, see Chabrier (*Compt. rend.* lxxviii. 1138; *Jahresb. f. Chem.* 1874, 1122; *Chem. Soc. J.* [1874], 1023).

An apparatus for measuring the pressure produced by the gases of burning powder in the chamber of the gun, and the pressure which the shot produces in driving the air before it, has been devised by Deprez a. Sebert (*Compt. rend.* lxxviii. 1835; *Jahresb. f. Chem.* 1874, 1120).

On the Composition and Analysis of Wood-Gunpowders, see F. W. Toms (*The Field*, 1878, No. 1336, p. 143; *Chem. Soc. J.* xxxiv. [1878], p. 923).

GURJUN BALSAM. From the residue left in the preparation of a large quantity of this balsam, Flüchiger obtained a neutral crystalline substance, $C^{24}H^{40}O^2$, which dissolved in petroleum-spirit, and separated therefrom in prismatic crystals, belonging to the triclinic system, and melting at 126° – 130° . This substance does not unite either with bases or with acids, but dissolves with reddish colour in sulphuric acid and is reprecipitated by water. It is not altered by fusion with potassium hydroxide. By dry distillation it yields an oil which is not affected by ferric chloride (*Arch. Pharm.* [3], xii. 58).

GYPSUM. *Occurrence and Formation.*—On the formation of Gypsum by the action of sulphur on calcium carbonate in presence of water, see CARBONATES (p. 415).

The gypsum and anhydrite of Airolo and Val Canaria have been described by K. von Fritsch (*Jahrb. f. Min.* vii. 299). These formations exhibit the tremendous force exerted by the expansion consequent on the conversion of anhydrite into gypsum, a force by which the crystals enclosed in the surrounding rock have been rent asunder. These crystals, which in the anhydrite are developed with perfect regularity, are found in the gypsum only as disintegrated fragments. Amongst these enclosed crystals are: bitter spar (4R.0R in the anhydrite, cleavage-rhombohedral in the gypsum); quartz; iron pyrites converted into brown iron ore; disthene (often superficially metamorphosed into transparent mica or talc); laminae of mica and talc (probably for the most part formed from disthene, as this mineral occurs frequently in the anhydrite, rarely in the gypsum, whereas for mica and talc the reverse holds good); very rarely tourmaline.

On the Crystalline Forms of Gypsum from Eichstadt near Merseburg, from the Pappelsberg in the Siebengebirge, and of gypsum twins from Eisleben, see Laspeyres (*Jahrb. f. Min.* 1876, 200; *Chem. Soc. J.* 1876, ii. 53); also Reusch (*Min. Mittheil.* 1876, 67).

Gypsum crystals from the miocene clay of Sütel in East Holstein, where they occur abundantly, are described by P. Klien (*Jahrb. f. Min.* 1876, 556). The usual forms of gypsum occur in this locality, but occasionally curious groups are found which bear a resemblance to twins, but are not so in reality. One crystal in these groups is larger in size than any of the rest, and at the same time serves as a support for the other crystals, which seem to radiate outwards from its centre. These crystals mostly enclose ferric oxide, which is distributed parallel to the various crystal faces, often assuming the appearance of a kernel in the crystal, enveloped by ferric oxide. Sometimes this deposition is repeated, giving rise to the formation of parallel zones.

On the 'Crystal-tectonic' of gypsum, see Klien (*ibid.* 563; *Chem. Soc. J.* 1877, i. 582).

Elasticity.—The coefficients of elasticity in gypsum are proportional to the cubes of the lengths of the axes of the coloured rings producible by pressure, and therefore also (see HMAT) to the cubes of the axes of the ellipses representing the distances to which a uniform temperature is extended in different directions by a given source of heat (Jannettaz, *Compt. rend.* lxxxii. 839).

Reaction with Sulphur.—In the extraction of sulphur from the ore by distillation, the sulphur is said by the workmen to be partly destroyed by the gypsum. This effect may be explained by the reaction represented in the equation $CaSO^4 + 2S = 2SO^2 + CaS$ (A. Cossa, *Gazz. Chim. ital.* 1874, 241).

Hardening of Burnt Gypsum.—Experiments by E. Landrin (*Ann. Chim. Phys.* [5], iii. 433) have shown that the rapidity with which burnt gypsum takes up water depends upon the temperature at which it has been burnt, and the time during which it has been exposed to that temperature. The best result is obtained by exposing the gypsum to a temperature of 100° – 300° , for 12 to 20 hours. Gypsum which has been heated to 400° likewise absorbs water quickly when stirred up with it; but hardens less, in proportion as it has been exposed to that temperature for a longer time. It is only at a cherry-red heat that gypsum loses the power of taking up water, but even at this temperature it does not give off sulphuric acid or experience any other chemical change.

The action of water on gypsum may be supposed to take place as follows. On coming in contact with water, part of the gypsum immediately becomes crystalline, while another part dissolves, and the liquid thus formed solidifies like a supersaturated solution, as soon as a crystal is formed by the evaporation of the water. The hardest product has the composition $CaSO^4 \cdot 2H^2O$, and contains 20 per cent. water. Ordinary burnt gypsum still retains 8 per cent. water, so that by stirring up the gypsum with

only 12 per cent. water, a paste should be formed which would solidify to a compact mass more quickly than any other. In practice, indeed, a paste thus composed is found to solidify too quickly, and for this reason it is customary to use at least 33 pts. water to 100 gypsum, and often a great deal more. The greater the quantity of water used, the looser is the solidified mass. To obtain a paste which solidifies slowly and ultimately becomes very hard, solutions of glue, dextrin, glycerin, &c., are used instead of water. Another method often adopted is to add a large quantity of water, and strew common salt on the surface of the solidifying mass; the salt takes water from the paste, which then solidifies quickly. The desired properties of slow solidification and great ultimate hardness are found united in the so-called *alumed gypsums* or *English cements*, which are made by steeping burnt gypsum for a few minutes in a 12–20 per cent. solution of alum, and then heating it to dull redness. It is commonly supposed that this process leads to the formation of double sulphates of calcium and alkali-metal. This view, however, is not confirmed by Landrin's analyses of a number of these gypsums, the results of which are shown in the following table:—

	French Cement.	English Cement		Stucco
		1	2	
Calcium Sulphate	96.75	98.19	98.02	98.55
Calcium Carbonate	1.05	0.41	0.37	0.36
Silica	0.72	—	0.42	0.51
Water	1.48	1.45	1.19	1.08

These numbers show that the constituents of the alum do not enter into the gypsum, as supposed by Gmelin and by Schott (*2nd Suppl.* 590). As massive native gypsum is for the most part rich in calcium carbonate (a sample from Paris was found to contain more than 4 per cent.); the treatment with alum serves merely to convert this calcium carbonate into sulphate. The alum for this purpose cannot be replaced by the simple sulphates of aluminium, potassium, sodium, ammonium, &c.; but the same effect may be produced by sulphuric acid. Crude gypsum, left in contact for some time with sulphuric acid of 8 to 10 per cent., and then burnt, yielded a preparation which exactly resembled alumed gypsum, and had the further advantage of a fine white colour, due to the destructive action of the sulphuric acid on admixed organic substances. The sulphuric acid cannot be replaced by hydrochloric acid, as the hygroscopic calcium chloride produced by the latter could not be completely removed. Gypsum which has been treated with sulphuric acid and afterwards burnt at a high temperature, behaves like strongly heated pure calcium sulphate; it dissolves in water more slowly than ordinary gypsum, does not become heated in combining with water, and solidifies less quickly than ordinary gypsum. The setting may be accelerated by heating the paste, or by using warm water for the mixing. If the gypsum be mixed with quick lime, the latter slakes during the mixing with water, thereby raising the temperature, and accelerating the evaporation, and consequently the setting of the gypsum. The resulting calcium hydroxide becomes saturated with carbonic acid, and thereby increases the solidity of the gypsum. The best proportion of lime to be added to the gypsum is 10 per cent.

H

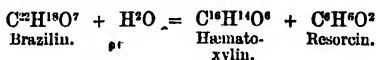
HÆMATEIN. See HÆMATOXYLIN.

HÆMATIN. See HÆMOGLOBIN.

HÆMATINONE. For the preparation of this red glass (iii. 3), the following process is recommended by Kayser (*Institut.* 1876, 279). Sixty parts of pure sand, 10 cupric oxide, 3 ferrosferic oxide, 10 calcined borax, and 10 calcined soda, are fused together at a high temperature, whereby the cupric oxide is reduced, after which the heat is lowered to dull redness, and kept at that point for some time. The product is a deep red glass flux covered over with a thin layer of cupric oxide glass. In Pottenkofer's process (iii. 3), which consists in adding cupric oxide mixed with ferrosferic oxide as a reducing agent to a lead glass, a partial reduction of the lead oxide takes place at the same time, whereby the glass acquires a brownish or even blackish colour.

HÆMATOIDIN. See HÆMOGLOBIN.

HÆMATOXYLIN, $C^{16}H^{14}O^6$. This compound is related to brazilin and resorcin in the manner shown by the equation :



(Liebermann a. Burg, *Deut. Chem. Ges. Ber.* x. 1883).

A solution of hæmatoxylin boiled in a platinum dish in an atmosphere free from ammonia acquires merely a brownish or brownish yellow colour; but, if boiled in a test-tube, it assumes in a few minutes a purple colour, showing that the glass has been decomposed, and has given up alkali to the water; for it is only in presence of oxygen and alkali that hæmatoxylin acquires the purple-red colour of hæmatein. On account of its sensitiveness to alkalis, hæmatoxylin may be very advantageously used as an indicator in acidimetry, especially for the estimation of non-volatile acids, which, by its aid, may be directly titrated with alkaline bicarbonates (O. Maschke, *Ber.* vii. 1535; *Arch. Pharm.* [3], vi. 34): see also H. W. Mitchell (*Amer. Chemist*, vi. 91).

According to Frébault (*J. Pharm. Chim.* [4], xxiii. 338), the red colour of hæmatein is destroyed by iodine or potassium iodide in presence of an alkali, and the reaction may be employed, best in very dilute solutions, for determining the amount of hæmatoxylin in logwood, and for the estimation of iodine.

HÆMIN. See the next article.

HÆMOGLOBIN AND ITS DERIVATIVES. *Reactions.*—Hæmoglobin is resolved by the action of iodine into hæmatin and globulin, as may be proved, both by comparing the absorption-spectrum after the addition of the iodine with that of pure hæmatin, and by observing the reaction itself under the microscope. In the latter case, not only is the actual precipitation of the hæmatin visible, but crystals of the iodide may be obtained by gently warming the substance on the microscope slip, with a drop of glacial acetic acid. These crystals belong to the rhombohedral system, and exhibit a stellate arrangement, often resembling the form of a Maltose cross (Husson, *J. Pharm. Chim.* [4], xxii. 326).

According to Rossbach (*N. Rep. Pharm.* xxii. 512), alkaloids increase the affinity of hæmoglobin for ozone, and retard the transference of the latter from hæmoglobin to other bodies. According to E. Schaer, on the other hand (*Deut. Chem. Ges. Ber.* vii. 1345), the separation of ozone from hæmoglobin is not retarded under normal circumstances by hydrochloride of quinine or by acetate of strychnine.

Estimation of Hæmoglobin.—Schutzenberger a. Küsler's method of estimating oxygen in blood by means of a standard solution of sodium hyposulphite, Na_2SO_3 , has been applied by Quinquaud (*Compt. rend.* lxxvi. 1489), to the determination of the amount of hæmoglobin contained in blood. The larger the quantity of hæmoglobin present, the greater is the amount of oxygen taken up by the blood when shaken up with air. 1,000 grams of human blood, containing 125 grams of hæmoglobin, absorb 200 c.c. oxygen. The blood of poultry takes up per litre 170 c.c. oxygen; it must, therefore, contain 82 grams of hæmoglobin per litre, a quantity agreeing exactly which Hoppe-Seyler calculated from the amount of iron in poultry blood.

On the Spectroscopic Estimation of Hæmoglobin in Human Blood, see Wiskemann (*Zeitschr. f. Biologie*, xii. 434; *Chem. Soc. J.* 1877, ii. 808).

Peroxyhæmoglobin.—By the action of acids on blood, a peroxidised product has been obtained, from which the oxygen can be again extracted by strong reducing agents, with formation of oxyhæmoglobin, and subsequently of reduced hæmoglobin. This substance, called *peroxyhæmoglobin* by Sorby, *methæmoglobin* by Hoppe-Seyler, *nitrilhæmoglobin* by Gamgee, may be prepared by acting upon blood with oxidising agents, such as potassium permanganate.

Peroxyhæmoglobin, in alkaline solution, has a three-banded spectrum. In acid solutions the spectrum has four absorption-bands similar to those of acid hæmatin. The most characteristic band has a wave-length of about 633, but by addition of acid to the blood, the position of the band changes with the intensity of the acidity, being moved towards the red end of the spectrum (Jaderholm, *Zeitschr. f. Biologie*, xiii. 255).

Hæmatin. Cazeneuve prepares pure hæmatin by dissolving 1 litre of defibrinated blood with 2 litres of a mixture of 3 parts ether and 2 parts alcohol of 85°. After twenty-four hours, the liquids having been stirred from time to time, the ethereal solution is decanted off and replaced by a fresh quantity of liquid containing 2 per cent. of oxalic acid. This dissolves out the colouring matters, and on the addition of ether holding ammonia gas in solution, to exact saturation of the oxalic

acid hæmatin is precipitated. The precipitate is washed successively with ether, alcohol, and water, and the residuo finally treated with ether saturated with hydrochloric, hydrobromic, or hydriodic acid, yields characteristic crystalline compounds (*J. Pharm. Chim.* [4], xxiv. 116).

Cazenave assigns to hæmatin the formula, $C^{88}H^{72}N^8Fe^2O^{10}$, agreeing with the latest determination by Hoppe-Seyler (*2nd Suppl.* 201). Its barium salt has the composition $C^{88}H^{68}BaN^8Fe^2O^{10}$ (*Bull. Soc. Chim.* [2], xxvii. 485).

When blood is treated with concentrated soda-solution, there is obtained after some time a bright red solution of reduced hæmatin, which subsequently coagulates. By dissolving this in water and treating it with dilute acetic acid, the colouring-matter is precipitated as oxyhæmatin. It may be somewhat purified by dissolving in ammonia-water, and reprecipitating with acetic acid; but it still contains albumin and a chlorinated compound insoluble in water.

Hæmatin, though usually insoluble in dilute as well as in concentrated acids, even hydrochloric acid, dissolves in concentrated acetic acid, and shows the same four-banded absorption-spectrum that it gives in acid, alcoholic, or ethereal solutions (*1st Suppl.* 355). A constant difference exists between the spectra of these solutions. In the alcoholic solution the absorption-band in the red is farther from Fraunhofer's line D than it is in the ethereal solution. In the former the centre of the band has a wave-length of about 627; in the latter, of about 638. This four-banded spectrum belongs, therefore, to hæmatin, and not, as stated by Preyer, to a colouring matter free from iron, the so-called hæmatoïn.

By evaporating the acid ethereal solution, yellowish-brown rhombic crystals and spindle-shaped thin tables are obtained. In a similar manner, by using sulphuric, hydrochloric, or other acid, crystals may be procured whose solubility in acids and alkalis corresponds with that of hæmatin crystals, as also do the absorption-spectra which are given by their solutions. Although these crystals contain iron, they are in all probability identical with Preyer's hæmatoïn-crystals and with Lehmann's hæmatin-crystals; whilst they are closely related to hæmin-crystals (Jaderholm, *Zeitschr. f. Biologie*, xiii. 193).

Hoppe-Seyler (*Deut. Chem. Ges. Ber.* vii. 1065) finds that the colouring matter which he obtained by the action of reducing agents on hæmatin (*2nd Suppl.* 202), is identical with the compound called urobilin by Jaffé and hydrobilirubin by Maly (*Ibid.* 190).

On crystalline compounds of Hæmatin with Acids, see Husson (*Compt. rend.* lxxxi. 477).

Hæmatoïdin (iii. 3). This substance is produced by treating blood with sodium borate and glacial acetic acid. Its crystals, apparently triclinic, exhibit under the microscope such varied and multiple forms of arrangement, that it is difficult to fix on any one of them as characteristic of the substance; it may be observed, however, that immediately surrounding the crystals, granulations of a reddish colour always occur, apparently resulting from the precipitation of the iron of the hæmatin at the moment of its conversion into hæmatoïdin (Husson, *J. Pharm. Chim.* [4], xxii. 326).

Hæmin. Thudichum & Kingzett (*Chem. Soc. J.* [1876], ii. 255) prepare this substance by a modification of Wittich's process, which consists in treating blood with seven times its bulk of a cold solution of potassium carbonate containing 1 part of the salt in 2 parts of water. The thick mixture is filtered on calico, then pressed in cloths, and afterwards treated with alcohol; the resulting solution, containing potassium carbonate is poured off, after standing for some time; and the residue, after being freed from liquor by pressing, is dried at the ordinary temperature. The product is then exhausted with warm absolute alcohol at a temperature not exceeding 40°, and the extracts so obtained are treated with an absolute alcoholic solution of tartaric acid. In this way the potash is precipitated and the hæmin remains dissolved, and on evaporation of the solution, is precipitated on cooling in very minute bluish-black crystals consisting of rhombic plates.

The analyses of this product yielded, as a mean result, 7.651 per cent. iron, 3.022 chlorine, and 0.608 phosphorus, whence it is inferred, that hæmin consists, not simply of hæmatin hydrochloride, as hitherto supposed, but of a mixture of that compound with hæmatin and a crystallisable phosphorised substance.

Hæmin heated in hydrochloric acid gas takes up 3.3 per cent. of its weight of that gas. It dissolves in a large quantity of nitric acid, without evolution of gas, forming a red-brown solution from which water throws down red flocks, leaving a nearly colourless liquid containing only a small quantity of iron, the greater portion of that metal being contained in the precipitate. The iron cannot be removed from hæmin by treatment with glacial acetic acid and citric acid, or with glacial acetic acid and benzene, the hæmin in fact not being altered by this treatment. The statement of

Paquelin a. Joly (*Compt. rend.* lxxviii. 1579), that the colouring matter of blood—which they call *hæmatosin*—does not contain iron, is therefore erroneous.

The liquid obtained by treating hæmin with acetic acid and benzeno yielded a phosphorised substance, forming with cadmium chloride a compound whose analysis showed that this phosphorised body is identical with the substance called *myelin* (q.v.) obtained from brain.

HAIR. The black pigment obtained by Hodgkinson a. Sorby from black and dark-brown feathers, is likewise found in hair of similar colour (p. 769).

HAIR-THAO. This substance, also called *gelose*, is used for finishing cotton goods. It is obtained from an alga, occurring abundantly in Cochin China and in the Mauritius, in the form of coarse, flat fibres, which are about 30 cm. long. It is without smell or taste, and consists of a transparent colourless mass, covered with a net of non-transparent veins. It is insoluble in cold water, and dissolves completely in hot water only after boiling for ten minutes, forming a transparent, thin, dirty-white solution, which on cooling deposits a yellowish-grey jelly, soluble on boiling. The jelly is neither acid nor alkaline, and does not show any signs of fermentation or putrefaction even when kept for about eight days. Thao dissolves in cold strong sulphuric, hydrochloric, or nitric acid, and is reprecipitated on adding water. To alkalis it behaves in the same way as to water, and is insoluble in alcohol both cold and hot.

With regard to its use for finishing cotton materials, experiments seem to show that it can be used only in hot solutions. With a dilution of 1 part of thao to 300 parts of water, the solution first begins to fix itself on the textures. With 1 part to 100 parts of water, the materials are rendered soft to the touch, and the texture gains in substance but not in stiffness. Thao fills the thread more completely than dextrin or starch, and produces a moister and finer texture. By adding glycerin to the thao-solution, a still softer and at the same time stronger material is obtained; the addition of talc, pipeclay, &c., yields a material of a fatty touch, and much finer and more delicate than that obtained from a dextrin or starch solution. Cotton finished with thao is not acted upon by cold water, as is the case with dextrin and starch; thao cannot, however, be used without ultramarine, as it gives to cotton a yellow tinge. With twilled materials thao draws the substance together, and thus prevents them from coming out well. It is only indeed for fine textures, which are to be rendered soft and firm to the touch, that the use of thao can be recommended. Where a heavy, stiff, and cheap finishing material is required, it cannot compete with dextrin or starch (*Heilmann, Dingl. Pol. J.* cxxiii. 522).

HALLOYSITE. A mineral resembling halloysite has been found by J. Rumpf (*Min. Mitth.* 1874, 282) on the Michaelerberg, near Tüffer in Styria, on the confines of the Leitha limestone and trachyte. It occurs in amorphous lumps of yellow, red, and brown colour. Analyses by R. Haller of an orange-red variety (a) and a liver-brown variety (b) gave the following results:

	SiO ^a	AlPO ^a	CaO	MgO	FeO ^a	H ^a O	Sp. gr.
a.	31.01	40.47	2.26	1.64	trace	24.27 = 99.65	2.06
b.	25.66	30.82	1.37	—	14.34	27.68 = 99.87	

HALOGENS. On the Mutual Displacement* of Halogen Elements, see CHEMICAL ACTION (p. 429). On the thermic phenomena accompanying these reactions, and the Oxidation of Haloid Salts, see HEAT.

Estimation of Halogen elements by means of Ammonium Thiocyanate (Volhard, *Liebig's Annalen*, etc. 1-61). The chlorine, bromine, or iodine is completely precipitated by adding an excess of a standard solution of silver nitrate, and the excess of silver is determined by adding a solution of a ferric salt and then a standard solution of ammonium thiocyanate, till the red colour of ferric thiocyanate shows itself, indicating the complete precipitation of the silver. A deci-normal solution of silver nitrate is used, and the thiocyanate solution is made to correspond with it by titration against it in presence of a ferric salt.

In applying this process to the estimation of chlorine, certain precautions are necessary, on account of the decomposing action exerted by silver chloride on the soluble thiocyanate. If the thiocyanate solution is added in excess to an ammoniacal solution of silver chloride, and the mixture is afterwards acidulated with nitric acid, the whole of the chlorine of the silver chloride passes into solution; but if the thiocyanate solution is dropped into a nitric acid solution containing silver nitrate and suspended silver chloride, together with the ferric salt as indicator, and the liquid is not shaken more than is necessary to secure complete mixture, the action on the silver chloride proceeds so slowly that the correctness of the result is not impaired. If, however, the agitation is violent and prolonged, the silver chloride, by decom-

posing a portion of the thiocyanate, will give results too low. It must further be remembered that after the pale-brown colour has once appeared, it is scarcely increased in intensity by further addition of the thiocyanate; hence it is necessary to acquire by practice the power of at once recognising the first appearance of the tint. The weighed metallic chloride is dissolved in 300 or 400 c.c. of water, mixed with 5 c.c. of cold iron-alum solution, and with sufficient nitric acid to remove the colour imparted by the ferric salt; deci-normal solution of silver nitrate is then added in slight excess, and the addition of the thiocyanate solution is at once proceeded with, the liquid being constantly shaken and stirred round to secure rapid mixture. The titration is finished when the liquid retains its pale-brown colour after standing still for ten minutes. The number of c.c. of silver nitrate solution used, diminished by the number of c.c. of thiocyanate solution, and multiplied by 0.00355, gives the weight of chlorine present in grams. If the weight of chlorine in solution is not known even approximately, a few drops of the standard thiocyanate solution may be added occasionally during the running in of the silver nitrate solution. As long as the silver solution is not in excess, the colour produced by the thiocyanate disappears slowly; but as soon as excess has been added, the colour caused by adding a drop of thiocyanate immediately vanishes, leaving the liquid milk-white. In calculating the result, the quantity of the standard thiocyanate thus used must be added to the quantity required for titrating the excess of silver, and the whole subtracted from the quantity of silver nitrate solution employed. Filtration from the silver chloride is not to be recommended, as it occasions waste of time; neither is the employment of an aliquot part of the clear liquid after subsidence advisable, since the accuracy of the result is thereby diminished. After a little practice results may be obtained of sufficient precision to be valuable for atomic weight determinations.

Bromine.—The action of silver bromide upon thiocyanate solution does not go nearly as far as that of silver chloride; in fact, experiment shows that the process applied to the estimation of bromine gives the final reaction at once and without difficulty, the results being very accurate. The point when excess of silver solution has been added can be judged with sufficient accuracy by the clarification of the liquid after brisk agitation.

Iodine.—Silver iodide does not exert any decomposing action on the thiocyanate; nevertheless the process is liable to be rendered inaccurate by silver iodide carrying down with it potassium iodide or silver nitrate, or both, and thus more or less withdrawing them from the reaction. To avoid this source of error, the following method of proceeding is necessary:—The iodide is dissolved in 300 or 400 times its weight of water in a stoppered bottle, and the silver solution is added to it until the precipitate coagulates on shaking; this shows that an excess of silver nitrate is present; 0.1 or 0.2 c.c. more of silver solution should then be added, and the liquid well shaken: by this means any unaltered alkaline iodide is converted into silver iodide. Either of two methods may then be used for completing the estimation: after addition of the ferric solution and nitric acid, thiocyanate solution is added until a decided coloration is obtained, and the liquid shaken until the colour disappears, the process being repeated until a faint colour remains after shaking; or excess of thiocyanate is at once added, the liquid well shaken, and the thiocyanate in excess titrated by silver solution, which should be added either until a faint brown colour remains, or else in slight excess, the excess being then titrated back by thiocyanate. The latter method is the more rapid, but the two give almost identical results.

Detection and Estimation of the Halogens when Thiocyanates are present.—To detect and separate the halogens, the thiocyanates must first be destroyed. To effect this, when a chloride is present, the precipitate obtained by excess of silver nitrate in the solution acidulated with nitric acid is filtered off, well-drained, and heated, together with the filter, with sulphuric acid diluted with half its volume of water, until the precipitate unites into black masses; a few drops of nitric acid are then added, and the heating continued. On diluting with water, all the chlorine remains as undissolved silver chloride, whilst the silver thiocyanate has been completely decomposed. Another plan is to dissolve 2 or 3 grams of the thiocyanate in 400 or 500 c.c. of water and heat on the water-bath, with occasional addition of nitric acid in small quantity as long as it produces any further reaction: the mixture is then further heated, the water lost by evaporation being replaced, until a drop no longer gives the thiocyanate reaction with a ferric solution decolorised by nitric acid. The liquid made alkaline with ammonia is evaporated to two-thirds of its bulk on the water-bath, and is then ready for precipitation by silver solution. By proceeding in this manner the thiocyanate is entirely destroyed, without loss of chlorine. If only a trace of chloride has to be detected, it is better to warm with nitric acid in a less dilute condition until evolution of gas ceases, add excess of sodium carbonate, evaporate to

dryness, ignite the residue, take up with warm water, and test with silver nitrate, after adding excess of nitric acid. The methods above described are inapplicable when bromine or iodine is present, as they would cause loss of these halogens. The silver precipitate may then be digested in a sealed tube with nitric acid for three or four hours at 160°, and the liquid diluted with water; or the substance may be fused with potassium nitrate and sodium carbonate, a large excess of the latter being used to avoid explosion. The latter method is better modified by mixing the substance with sodium carbonate, both being perfectly dry, and gradually dropping the mixture into fused potassium nitrate.

Separation of Chloride and Iodide.—If a mixture of silver chloride and silver iodide is mixed with ammonia in excess and sufficient ammonium thiocyanate, and digested at ordinary temperatures for an hour, the chloride is completely decomposed, the iodide remaining quite unaltered. On acidifying with nitric acid and washing the precipitate, the chloride will be contained entirely in the filtrate together with thiocyanate; the iodide will remain as insoluble silver iodide mixed with silver thiocyanate. After destroying the thiocyanate in the filtrate and precipitate respectively by the methods above given, the chloride may be titrated by the thiocyanate process, and the iodide weighed.

Estimation of the Halogens in Organic Compounds.—The thiocyanate method is remarkably well suited to the estimation of halogens in organic substances, the organic matter being previously destroyed and the halogen brought into the form of an inorganic compound by either of the ordinary methods,* provided no loss of the halogen is incurred. Combustion with lime free from halogens is quite trustworthy; but Volhard prefers mixing the substance with forty times its weight of a mixture of sodium carbonate with twice its weight of potassium nitrate, and burning in a covered crucible, or in an inclined combustion tube, according to the nature of the substance. These salts are chosen as being easily obtained free from halogens. In the case of very volatile substances, a layer of potassium nitrate is placed above the mixture containing the substance, and is fused before heating the mixture.

Another method of estimating the halogen elements in organic compounds is given by E. Kopp (*Deut. Chem. Ges. Ber.* viii. 769). The substance mixed with pure *ferrie oxide* is introduced into a combustion-tube about 60 cm. long and 5 to 6 mm. in diameter, so as to form a loose layer from 12 to 13 cm. long; above this are placed several coils of fine pianoforte wire, and the rest of the tube is filled with dehydrated sodium carbonate. The part of the tube containing the iron wire is then heated to redness, and the heating is gradually extended to the closed end of the tube. By this treatment, the organic substance mixed with the ferric oxide is completely decomposed, and the halogens are retained in the form of iron-compounds having but little volatility. The tube is then left to cool, cleaned on the outside, and cut into fragments on a sheet of paper; the fragments are boiled with distilled water; the filtered liquid is acidulated with nitric acid; and the halogen-element contained in it is precipitated with silver nitrate in the usual way. This mode of treating the contents of the tube is apt however to be attended with loss, partly from the flying off of small glass splinters, and partly from the deliquescence of some of the halogen salts, in consequence of which they are absorbed by the paper. To obviate these sources of error, Klobukowski (*Ber.* x. 290) modifies the latter part of the manipulation by removing the tube from the furnace while it is still hot (but no longer red-hot), wiping it rapidly with a dry cloth, closing it with the finger, and plunging it into a tall beaker one-fifth full of distilled water, whereby the hot part of the tube is broken into small fragments. The cold part containing sodium carbonate is then washed out with distilled water; the contents of the beaker, together with the washings, are heated in the water-bath for 30 or 40 minutes; the liquid is filtered; the residue washed with hot water; and the solution of sodium chloride, bromide, or iodide thus obtained is precipitated with silver nitrate.

HASCHISCH. This substance, obtained from Indian hemp (*Cannabis indica*), has been examined by Probraschensky (*Russ. Zeitschr. Pharm.* 1876, 705), who has obtained from it, together with resinous substances, a volatile base which in external appearance and the properties of its salts bears a strong resemblance to nicotine. The same base is obtained by distilling the herb with water.

HATCHETTOLITE. See NIOBATES.

* Carius's method of heating the organic substance with nitric acid in a sealed tube, modified by addition of a known quantity of silver nitrate, does not give good results, as the violent escape of gas which takes place on opening the tube is apt to occasion loss of liquid; and moreover the silver precipitate, at the high temperature of the reaction, is brought into a very dense state, which renders the washing out of the excess of silver nitrate a matter of great difficulty. A further objection to the process is that it affords no means of ascertaining when the decomposition is complete.

HAUYN. A microchemical reaction of minerals belonging to the hauyn family has been observed by A. Knop (*Jahrb. f. Min.* 1875, 74). When a thin section of a rock in which these minerals are present is heated for a few minutes in a platinum crucible with flowers of sulphur, the cross sections of hauyn and nosean exhibit a fine sky-blue colour. Whether this reaction is likewise exhibited by sodalite has not yet been ascertained, but it does not occur with the feldspars, or with nephelin, leucite, apatite, or natrolite.

HEAT. THERMOMETRY and CALORIMETRY. Zero-point of Thermometers.—For the determination of this point of the scale, C. Tellier (*Compt. rend.* lxxv. 572) recommends the immersion of the thermometer in water which has been cooled down without solidifying, to a few degrees below 0° , and then made to freeze by agitation, or by the introduction of a fragment of ice, as the water is thereby brought back exactly to 0° , whereas water obtained by the melting of ice may have a temperature somewhat higher than the ice itself. B. F. Craig, on the other hand (*American Chemist*, 1875, iii. 325), objects to this method on the ground that the true zero-point is not the freezing point of water, but the melting point of ice; and this may be determined by plunging the instrument into melting snow, taking care that no water collects round the bulb. The excess of temperature sometimes indicated by thermometers is, for the most part, due, not to an originally incorrect determination of the zero-point, but to a contraction of the bulb which takes place in course of time.

T. M. Morgan (*Chem. News*, xxix. 111) observed that a thermometer which had been used for several days in distillations, and completely immersed in the vapour, showed temperatures 3° too low, in consequence of evaporation and precipitation of a portion of the mercury on the upper part of the tube; but by allowing the mercury to run down to the end of the tube, the condensed portion was re-collected, and the instrument then gave correct indications. In Geissler's thermometers a small quantity of hydrogen is enclosed, in order to prevent the volatilisation of the mercury.

On the determination of the Freezing and Boiling Points, see also Wiebe, as reported by Lowenherz (*Ber.* 1877, 469–474, 647; *Jahresb. f. Chem.* 1877, 91).

Differential Thermometers.—L. Pfaundler (*Wien. Acad. Ber.* [2te Abth.], lxxii., Doc. IIeft.) explains the theory of the modified forms of Berthelot's differential air-thermometer (1st Suppl. 663), which he introduced some years ago, in order to eliminate the influence of barometric changes on the indications of the instrument. The parts common to the several forms are as follows: In the space whose temperature is to be determined, is a glass vessel V, communicating by means of a vertical capillary pressure-gauge with a second vessel V', whose temperature is known and is kept constant. At 0° , the vessels V and V' contain portions of air having a definite ratio of pressure. As long as this state of things is maintained, and the temperature in V' remains constant, the temperature to be measured is determined solely by the difference of height h of the two columns of mercury. This being known, it is easy to deduce a general formula applicable to all thermometers of this kind, the individual forms of which are included in it as special cases.

Let t be the unknown ordinary temperature of the vessel V.

T " absolute " " " V.

t' the known ordinary temperature of the vessel V'.

T' " absolute " " " V'.

P the gas-pressure at 0° in the vessel V (in millimeters).

P' " " " " V'

h the observed difference of height, at t° , of the two mercury columns.

The sign of h is to be considered positive when the pressure of the mercury-column is directed on the air in V.

We have then $P(1 + \alpha t) = P'(1 + \alpha t') + h$: whence, in centigrade temperatures,

$$t = \frac{P'}{P} t' + \frac{1}{\alpha P} + \frac{1}{\alpha} \left(\frac{P'}{P} - 1 \right)$$

or, more simply, in absolute temperatures,

$$T = \frac{P'}{P} T' + \frac{1}{\alpha P}$$

Since $\frac{P'}{P}$, $\frac{1}{\alpha P}$, and $\frac{1}{\alpha} \left(\frac{P'}{P} - 1 \right)$ are magnitudes which remain constant so long as the filling of the instrument does not vary, it is clear that the absolute temperature to be measured is the sum of two quantities, one of which is proportional to the

absolute temperature of the space V' , the other to the difference of height h . The preceding formula shows that in all cases the delicacy of the instrument, *i.e.* the increase of h for a rise of temperature of 1° , depends alone on P , and therefore on a quantity quite within the control of the instrument-maker. Pfaunder's paper contains a full description of the several constructions, and gives the proportions of filling for $P = P'$, $P < P'$, $P > P'$, and $P = 0$.

PYROMETERS. *Siemens's Electrical Pyrometer* depends for its action on the regular increase of electric resistance in a metallic conductor, produced by rise of temperature. It consists essentially of a platinum spiral, duly protected, and so arranged that its resistance to an electric current can be measured while it is exposed to the temperature to be estimated (*Dingl. pol. J.* ccix. 419).

From experiments conducted by a Committee of the British Association, and reported by G. C. Foster, these pyrometers, after once or twice heating, exhibit an increase of resistance, but afterwards do not appear to undergo further alteration (*Chem. News*, xxviii. 173). From further experiments conducted by Foster, however, it appears that when the platinum spiral is protected by an iron tube, the instrument does not give constant results, on account of the great increase of resistance produced by heating. If, on the other hand, the use of iron be avoided, the indications of the instrument are sufficiently exact for most industrial applications. A full description, with drawings, of the electric pyrometer is given by Siemens (*Dingl. pol. J.* ccxvii. 291-297).

An *air-pyrometer*, provided with a condensed air pressure-gauge, is described by G. Codazza (*Dingl. pol. J.* cex. 255).

A *calorimetric pyrometer*, for the measurement of high temperatures, is described by J. Salleron (*Monit. Scient.* [3], iii. 841; *Chem. News*, xxviii. 77). A cylinder of copper or platinum, surrounded by an envelope of the same metal to diminish the loss of heat by conduction or radiation, is raised to the temperature to be determined, and then quickly plunged into the water of a calorimeter. The temperature of the water is then noted, and the temperature to be determined is calculated from it by known methods.

An *acoustic pyrometer*, for measuring changes of temperature by the alterations thence resulting in the number of wave-lengths of the air in tubes, is described by A. M. Meyer (*Pogg. Ann.* cxlviii. 287; *Phil. Mag.* [4], xlv. 18).

A modification of Bunsen's ice-calorimeter (2nd Suppl. 595), in which common ice can be used instead of pure snow, and the observations are made with greater facility, is described by Schüller a. Wartha (*Ber.* viii. 1011).

Berthelot (*Ann. Chim. Phys.* [5], x. 168, 391, 447-458) describes a number of calorimetric instruments for measuring the quantities of heat given out in the absorption of gases by liquids; also an apparatus for determining the specific heat of liquids (*ibid.* xii. 559).

SPECIFIC HEAT.

a. Of Solids.—(1). Carbon, Boron, and Silicon.—H. F. Weber has continued his researches on the specific heat of carbon at different temperatures (2nd Suppl. 596), and has made similar observations on the specific heats of boron and silicon (*Jahresb. f. Chem.* 1874, 64).

The following table exhibits the true specific heats γ_t of these elements, deduced from the mean results of the several groups of experiments, together with a comparison of the mean heat-capacities C_{0-t} of lamellar graphite and amorphous charcoal:

Diamond	Graphite	Crystallised Boron	Crystallised Silicon
$\gamma_{-50.5} = 0.0635$	$\gamma_{-50.3} = 0.1138$	$\gamma_{-39.6} = 0.1915$	$\gamma_{-39.8} = 0.1360$
$\gamma_{-10.6} = 0.0955$	$\gamma_{-10.7} = 0.1437$	$\gamma_{26.6} = 0.2382$	$\gamma_{21.6} = 0.1697$
$\gamma_{10.7} = 0.1128$	$\gamma_{10.8} = 0.1604$	$\gamma_{76.7} = 0.2737$	$\gamma_{57.1} = 0.1833$
$\gamma_{33.4} = 0.1318$	$\gamma_{61.3} = 0.1990$	$\gamma_{125.4} = 0.3069$	$\gamma_{86.0} = 0.1901$
$\gamma_{58.3} = 0.1532$	$\gamma_{138.5} = 0.2542$	$\gamma_{177.2} = 0.3378$	$\gamma_{128.7} = 0.1964$
$\gamma_{85.5} = 0.1765$	$\gamma_{201.6} = 0.2966$	$\gamma_{233.2} = 0.3663$	$\gamma_{184.3} = 0.2011$
$\gamma_{140.0} = 0.2218$	$\gamma_{249.3} = 0.3250$		$\gamma_{239.4} = 0.2029$
$\gamma_{206.1} = 0.2733$			
$\gamma_{247.8} = 0.3026$			
$\gamma_{306.7} = 0.4408$			
$\gamma_{306.3} = 0.4489$			
$\gamma_{385.0} = 0.4589$			
Lamellar Graphite	Dense amorphous charcoal	Porous Wood-charcoal	
$C_{0-21.6} = 0.1605$		$C_{0-23.5} = 0.1653$	
$C_{0-99.9} = 0.1904$	$C_{0-99.9} = 0.1906$	$C_{0-99.2} = 0.1935$	
$C_{0-225.3} = 0.2350$	$C_{0-225.3} = 0.2340$	$C_{0-223.6} = 0.2385$	

The facts and general points of view established by the experimental results above recorded, may be arranged in the following groups:

(1). The specific heats of the isolated elements, carbon, boron, and silicon, vary to an extraordinary amount with change of temperature. From the lowest attainable temperatures, the specific heats of these elements increase regularly as the temperature rises, till, from a certain temperature upwards, they remain nearly constant. For carbon, this temperature is near 600° , for silicon about 200° . For a rise of temperature from -50° to 600° , the specific heat of carbon increases to seven times, and that of boron to 2.5 times its value, at the lower temperature. The specific heats of the elementary bodies are indeed, for the most part, not constant quantities, but are influenced by the physical state of the elements as much as by their chemical nature. The assumption hitherto made by physicists that the influence of temperature on the specific heat of the elements is quite insignificant, and easily explicable by the alterations of molecular structure produced by heat, and that, in regard to the fundamental law relating to the specific heats of the elements, it may be completely neglected, must, for the future, be regarded as untenable.

(2). The final and nearly constant values which the specific heats of carbon, boron, and silicon attain with increasing temperature are, in round numbers, 0.46 for C, 0.50 for B, and 0.205 for Si. The products of these numbers into the atomic weights of the three elements deduced from vapour-density determinations, are 5.5, 5.5, and 5.8, numbers which approach nearly to the atomic heats of the metals and of the other solid non-metallic bodies (aluminium 5.7, sulphur 5.5). Carbon, boron, and silicon enter therefore at certain temperatures into the range of the Dulong-Petit law, and conform to it at all higher temperatures. This law of the specific heats of the solid elements may now therefore be regarded as universal. The usual mode of stating it requires, however, to be somewhat altered, perhaps as follows:

The specific heats of the solid elements vary with the temperature; and for each element there is in the scale of temperature a certain point t° , above which the variation of the specific heat with increasing temperature becomes quite insignificant.—The product of the atomic weight into that value of the specific heat which holds good for temperatures above t° , yields, for all the solid elements, a nearly constant value comprised between the limits 5.5 and 6.5. The smallest quantities of the elements carbon, boron, and silicon, hitherto found to enter into the molecules of their gaseous compounds, viz. 12, 11, and 28, are not multiples of the atomic weights of these elements, but the true atomic weights themselves.

(3). All the opaque modifications of carbon (the graphitic, dense and porous forms) exhibit the same specific heat; the opposite assumption hitherto admitted rests on defective investigations. Below red heat there exist in a thermic point of view, only two allotropic modifications of carbon, the transparent and the opaque. The specific heats of these two modifications differ the more widely as the temperature is lower, and as the temperature rises they steadily approach one another, till at 600° and above they become equal. From red heat upwards, there are, so far as specific heat is concerned, no allotropic modifications of carbon; from the point of the temperature-scale at which the optical difference between the two modifications of carbon vanishes, the thermic difference likewise disappears.

Mixter a. E. S. Dana (*Liebig's Annalen*, clxix. 388), by means of Bunsen's ice-calorimeter, find, for the specific heat of boron, the number 0.2518; of silicon 0.1710; of zirconium 0.6660 [at what temperatures?]

Schüller a. Wartha, by means of their ice-calorimeter (p. 925), have found the specific heat of distilled zinc = 0.09393; that of artificial titanite anhydride = 0.1785 and 0.1779, and that of native rutile = 0.1737.

On the specific heats of Cerium, Lanthanum, and Didymium, see p. 418; of Glucinum, p. 868.

2. Of Alloys.—The specific heats and expansions of several fusible alloys have been determined by W. Spring (*Ann. Chim. Phys.* [5], vii. 178–228), with the following results. The specific gravities are reduced to the vacuum and to 4° ; the volumes to 0° .

Rose's Alloy.

Bi = 48.9; Sn = 23.6; Pb = 27.6 per cent.—Sp. gr. = 9.5125.

Temperature	Volume	Specific Heat
29.0°	1.00682	0.0474
38.5°	1.01295	0.0562
68.2°	1.00700	0.0545
100.0°	1.04500	0.0881

D'Arcet's Alloy.

Bi = 49.2; Sn = 21.2; Pb = 27.6 per cent.—Sp. gr. = 9.6401.

Temperature	Volume	Specific Heat
29.0°	1.01485	0.0621
35.0°	1.01825	—
41.5°	1.01600	0.0528
56.5°	1.02493	0.0650
101.3°	1.09980	0.8901

Lipowitz' Alloy.

Bi = 50.0; Sn = 12.8; Pb = 26.9; Cd = 10.4 per cent.—Sp. gr. = 9.7244.

Temperature	Volume	Specific Heat
28.0°	1.03210	0.0634
50.0°	1.00115	0.0544
90.5°	1.05042	0.0625

Wood's Alloy.

Bi = 55.7; Sn = 13.7; Pb = 13.7; Cd = 16.8 per cent.—Sp. gr. = 9.1106.

Temperature	Volume	Specific Heat
53.25°	1.00265	0.0575
93.0°	1.03735	0.0918

These numbers show that the alterations of specific heat in the alloys mentioned follow the alterations of volume produced by heat, independently of the temperature.

β. Specific Heat of Liquids. 1. Of Mercury. According to A. Winkelmann, *Pogg. Ann.* (clix. 152–165), the specific heat of mercury diminishes with rise of temperature. Between 49.6° and 19.7° it is 0.03312, and between 142.2° and 25.5° it is 0.03278. Calculating from these numbers the values of the constants in the formula, $C = C + at$, we find $C = 0.03336$; $a = -0.0000069$.

2. Of Water. J. Bosscha (*Pogg. Ann.* 1874; *Jahrbld.* 549–557) has endeavoured, by means of his own observations on the expansion of mercury (*Pogg. Ann. Ergänzbd.* v. 276; *Jahresh f. Chem.* 1869, 82, 83) and the detailed account of Regnault's observations, to eliminate from the experiments of the latter on the specific heat of water (iii. 34), the errors which he supposes to have arisen from uncertainties in the temperature-determinations on which the results were founded. The following table exhibits a comparison of Regnault's values with Bosscha's corrected values, and likewise those calculated from the formula:

$$C = 1 + \delta \left(\frac{T + t}{2} - 18 \right)$$

in which, as a mean calculated from forty of Regnault's observations, $\delta = 0.0022$.

Limits of Temperature	Mean Sp. Heat according to Regnault	Corrected Sp. Heat	Calculated from the formula	Difference
110°–20°	1.0054	1.0112	1.0103	+ 0.0009
119°–23°	1.0063	1.0123	1.0117	+ 0.0005
134°–25°	1.0068	1.0126	1.0137	– 0.0011
157°–26°	1.0085	1.0148	1.0163	– 0.0015
173°–24°	1.0114	1.0176	1.0179	– 0.0002
188°–29°	1.0157	1.0215	1.0200	– .0015

These numbers show that the formula, $c = 1 + 0.0022 (t - 18)$, represents the observations as nearly as can be expected from these experiments. If it be assumed

that the specific heat of water in the neighbourhood of the freezing point varies according to the same law as at other temperatures, the preceding formula may be replaced, with sufficient exactness, by $c = 0.00022t$, in which the specific heat of water at 0° is taken as unity.

3. Of Saline Solutions. Elaborate experiments on the specific heat of saline solutions have been made by C. Marignac (*Ann. Chim. Phys.* [5], viii, 410), in continuation of those already reported (*2nd Suppl.* 601). The results are given in the following table:

Chlorides, Bromides, Iodides								
Formula	Mol. wt.	Specific Heat			Molecular Heat			Temp.
		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
H ⁺ Cl ⁻	72.9	0.8787	0.9336	0.9650	855	1749	3544	20-24°
K ⁺ Cl ⁻	149.2	0.8312	0.9032	0.9483	872	1760	3555	17-22°
K ⁺ Br ⁻	238.2	0.8344	0.9055	0.9490	876	1765	3558	20-51
K ⁺ I ⁻	332	0.7691	0.8643	0.9250	875	1762	3550	20-51
K ⁺ I ⁻	332	0.7153	0.8301	0.9063	881	1770	3563	20-51
Na ⁺ Cl ⁻	117	0.8760	0.9280	0.9596	891	1779	3566	16-20
Na ⁺ Br ⁻	206	0.8779	0.9304	0.9623	893	1783	3577	22-52
Na ⁺ I ⁻	300	0.8092	0.8864	0.9388	895	1778	3573	20-52
Na ⁺ I ⁻	300	0.7490	0.8499	0.9174	899	1785	3578	20-51
N ⁺ H ⁺ Cl ⁻	106.9	0.8850	0.9382	0.9670	891	1789	3585	20-52
CaCl ²	110.9	0.8510	0.9154	0.9554	860	1749	3546	20-25
CaCl ²	110.9	0.8510	0.9174	0.9550	860	1753	3544	21-51
SrCl ²	158.4	0.8143	0.8942	0.9430	862	1751	3544	21-26
SrCl ²	158.4	0.8165	0.8950	0.9424	864	1753	3542	19-51
BaCl ²	208	0.7799	0.8751	0.9319	864	1737	3549	22-27
BaCl ²	208	0.7805	0.8762	0.9325	865	1759	3551	21-52
MgCl ²	95.4	0.8607	0.9245	0.9581	857	1752	3540	18-23
MgCl ²	95.4	0.8665	0.9235	0.9594	862	1750	3547	22-52
MnCl ²	125.9	0.8510	0.9154	0.9526	873	1763	3549	19-52
NiCl ²	130	0.8310	0.9017	0.9541	856	1740	3525	24-55
CuCl ²	134.2	0.8642	0.9200	0.9563	894	1778	3571	19-51
ZnCl ²	136.3	0.8842	0.9330	0.9590	916	1807	3583	19-51
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
N ⁺ H ⁺ Cl ⁻	106.9	—	—	0.8134	—	—	453	20-52°
CaCl ²	110.9	0.6176	0.6741	0.7538	179.6	256.7	422.8	21-51
MgCl ²	95.4	—	0.6824	0.7716	—	249.4	421	22-52
NiCl ²	130	—	—	0.7351	—	—	426.4	24-55
CuCl ²	134.2	0.6241	—	0.7790	196.1	—	455	19-51
ZnCl ²	136.3	0.6212	0.7042	0.7960	196.5	286.1	466.7	19-51

Nitrates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
H ⁺ O.N ⁺ O ⁻	126	0.8752	0.9273	0.9618	898	1786	3584	21-52°
K ⁺ O.N ⁺ O ⁻	202.4	0.8320	0.9005	0.9430	917	1803	3586	18-23
K ⁺ O.N ⁺ O ⁻	202.4	0.8335	0.9028	0.9475	919	1808	3603	22-52
Na ⁺ O.N ⁺ O ⁻	170.2	0.8692	0.9220	0.9545	930	1816	3599	18-23
Na ⁺ O.N ⁺ O ⁻	170.2	0.8712	0.9220	0.9576	932	1816	3610	22-52
N ⁺ H ⁺ O.N ⁺ O ⁻	160	0.8797	0.9293	0.9610	932	1821	3614	20-52
Ag ⁺ O.N ⁺ O ⁻	340	0.7505	0.8491	0.9131	931	1817	3598	25-52
CaO.N ⁺ O ⁻	164	0.8471	0.9116	0.9511	901	1790	3580	20-25
CaO.N ⁺ O ⁻	164	0.8463	0.9110	0.9510	900	1789	3580	21-51
SrO.N ⁺ O ⁻	211.5	—	0.8903	0.9400	—	1791	3583	21-26
SrO.N ⁺ O ⁻	211.5	0.8169	0.8905	0.9392	908	1791	3580	19-51
BaO.N ⁺ O ⁻	261	—	—	0.9304	—	—	3592	21-26
BaO.N ⁺ O ⁻	261	—	—	0.9294	—	—	3588	19-51
PbO.N ⁺ O ⁻	331	0.7507	0.8510	0.9162	924	1813	3602	21-26
PbO.N ⁺ O ⁻	331	0.7500	0.8507	0.9173	923	1813	3606	18-51
MgO.N ⁺ O ⁻	148.6	0.8501	0.9133	0.9546	891	1780	3578	17-22
MgO.N ⁺ O ⁻	148.6	0.8517	0.9145	0.9537	893	1782	3575	21-52

Nitrates.—Continued.

Formula	Mol. wt.	Specific Heat			Molecular Heat			Temp.
		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
MnO.N ² O ³	179	0.8320	0.9027	0.9473	898	1786	3580	19-51°
NiO.N ² O ³	183	0.8228	0.8949	0.9409	891	1774	3559	24-56
CuO.N ² O ³	187.2	0.8256	0.8992	0.9475	898	1788	3588	18-50
ZnO.N ² O ³	189.4	0.8234	0.8990	0.9461	897	1789	3585	20-52
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
H ² O.N ² O ³	126	0.7212	—	0.8043	220.7	—	463.3	21-52
Na ² O.N ² O ³	170.2	—	0.7299	0.7946	—	321	492.6	22-52
N ² H ⁴ O.N ² O ³	160	0.6942	0.7437	0.8090	236	319.8	493.5	20-52
CaO.N ² O ³	164	0.6255	0.6856	0.7597	215.2	297.5	466.5	21-51
MgO.N ² O ³	148.6	—	0.6777	0.7568	—	283.7	453	21-52
NiO.N ² O ³	183	—	—	0.7171	—	—	454	24-55
ZnO.N ² O ³	189.4	0.5906	0.6410	0.7176	218.2	294.5	459	20-52
H ² O.N ² O ³ + 5 Aq.;		Sp. Heat 0.6551;			Molec. Heat 141.5			
N ² H ⁴ O.N ² O ³ + 5 Aq.;		" 0.6102			" 152.5			

Sulphates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
H ² O.SO ³	98	0.9155	0.9545	0.9747	914	1812	3604	16-20°
K ² O.SO ³	174.2	—	0.8965	0.9434	—	1770	3500	18-23
		—	0.9020	0.9463	—	1781	3571	19-52
Na ² O.SO ³	142	0.8753	0.9250	0.9576	912	1796	3583	19-24
		0.8784	0.9270	0.9596	915	1800	3591	21-52
N ² H ⁴ O.SO ³	132	0.8789	0.9330	0.9633	907	1802	3595	19-51
MgO.SO ³	120.5	0.8654	0.9225	0.9547	883	1772	3552	19-24
		0.8690	0.9230	0.9550	887	1773	3553	22-52
MnO.SO ³	151	0.8440	0.9125	0.9529	887	1780	3574	19-51
NiO.SO ³	155	0.8371	0.9102	0.9510	883	1779	3571	25-56
CuO.SO ³	159.3	0.8411	0.9084	0.9503	891	1780	3572	18-23
		0.8520	0.9148	0.9528	902	1792	3582	22-53
ZnO.SO ³	161.4	8420	0.9106	0.9523	894	1786	3582	20-52
GO.SO ³	105.3	0.9009	0.9457	0.9703	906	1802	3595	21-52
Al ³ O.SO ³	114.3	0.9041	0.9465	0.9722	917	1812	3611	21-53
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
Na ² O.SO ³	142	—	—	0.8191	—	—	485	21-52°
N ² H ⁴ O.SO ³	132	—	0.7385	0.8030	—	297	467.3	19-51
GO.SO ³	105.3	—	—	0.8285	—	—	460	21-52
Al ³ O.SO ³	114.3	—	—	0.8400	—	—	474	21-53

Chromates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
H ² O.CrO ³	118.5	0.8962	0.9419	0.9698	913	1807	3606	21-53°
K ² O.CrO ³	194.8	0.8105	0.8896	0.9407	887	1775	3570	20-51
Na ² O.CrO ³	162.6	0.8560	0.9134	0.9511	909	1793	3579	21-52
N ² H ⁴ O.CrO ³	152.5	0.8767	0.9304	0.9630	923	1817	3613	22-53
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
H ² O.CrO ³	118.5	0.6964	—	0.8251	207.9	—	469	21-53°
Na ² O.CrO ³	162.6	—	—	0.7810	—	—	478.4	21-52
N ² H ⁴ O.CrO ³	152.5	—	—	0.7967	—	—	480	21-52

Phosphates, Arsenates, Pyrophosphates, Metaphosphates.

Formula	Mol. wt.	Specific Heat			Molecular Heat			Temp.
		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
$\frac{1}{2} \left(\text{P}^2\text{O}^5 \cdot \begin{Bmatrix} \text{Na}^2\text{O} \\ 2\text{H}^2\text{O} \end{Bmatrix} \right)$	120	0.9070	0.9499	0.9704	925	1823	3610	24-55°
$\frac{1}{2} \left(\text{As}^2\text{O}^5 \cdot \begin{Bmatrix} \text{Na}^2\text{O} \\ 2\text{H}^2\text{O} \end{Bmatrix} \right)$	164	0.8707	0.9264	0.9595	926	1819	3611	26-57
$\frac{1}{2} \left(\text{P}^2\text{O}^5 \cdot \begin{Bmatrix} 2\text{Na}^2\text{O} \\ \text{H}^2\text{O} \end{Bmatrix} \right)$	142	—	0.9345	0.9617	—	1815	3598	23-54
$\frac{1}{2} \left(\text{As}^2\text{O}^5 \cdot \begin{Bmatrix} 2\text{Na}^2\text{O} \\ \text{H}^2\text{O} \end{Bmatrix} \right)$	186	0.8550	0.9112	0.9500	928	1809	3596	25-56
$\frac{1}{2} (\text{P}^2\text{O}^5 \cdot 2\text{Na}^2\text{O})$	133	—	0.9375	0.9666	—	1812	3608	24-55
$\frac{1}{2} (\text{P}^2\text{O}^5 \cdot \text{Na}^2\text{O})$	102	0.9129	0.9525	0.9761	914	1811	3613	24-55
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
$\frac{1}{2} \left(\text{P}^2\text{O}^5 \cdot \begin{Bmatrix} \text{Na}^2\text{O} \\ 2\text{H}^2\text{O} \end{Bmatrix} \right)$	120	—	—	0.8444	—	—	481.3	24-55
$\frac{1}{2} \left(\text{As}^2\text{O}^5 \cdot \begin{Bmatrix} \text{Na}^2\text{O} \\ 2\text{H}^2\text{O} \end{Bmatrix} \right)$	164	—	—	0.7884	—	—	484	26-57
$\frac{1}{2} (\text{P}^2\text{O}^5 \cdot \text{Na}^2\text{O})$	102	—	—	0.8495	—	—	469	24-55

Acetates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
$\text{H}^2\text{O} \cdot \text{C}^4\text{H}^4\text{O}^2$	120	0.9568	0.9799	0.9874	976	1875	3673	21-52
$\text{K}^2\text{O} \cdot \text{C}^4\text{H}^4\text{O}^2$	196.3	0.8572	0.9170	0.9550	940	1831	3625	20-51
$\text{Na}^2\text{O} \cdot \text{C}^4\text{H}^4\text{O}^2$	164	{ 0.9026 0.9037	{ 0.9414 0.9430	{ 0.9644 0.9687	{ 960 962	{ 1849 1852	{ 3630 3646	{ 20-25 19-52
$\text{CaO} \cdot \text{C}^4\text{H}^4\text{O}^2$	158	{ 0.8914 0.8959	{ 0.9362 0.9392	{ 0.9670 0.9663	{ 943 948	{ 1833 1839	{ 3634 3631	{ 20-25 22-52
$\text{SrO} \cdot \text{C}^4\text{H}^4\text{O}^2$	205.5	0.8505	0.9127	0.9513	940	1830	3620	20-52
$\text{BaO} \cdot \text{C}^4\text{H}^4\text{O}^2$	255	0.8166	0.8911	0.9396	943	1831	3622	19-52
$\text{PbO} \cdot \text{C}^4\text{H}^4\text{O}^2$	325	{ 0.7925 0.7939	{ 0.8797 0.8808	{ 0.9322 0.9327	{ 971 973	{ 1869 1872	{ 3659 3661	{ 21-26 18-51
$\text{MgO} \cdot \text{C}^4\text{H}^4\text{O}^2$	142.6	0.9055	0.9473	0.9712	944	1840	3635	21-52
$\text{MnO} \cdot \text{C}^4\text{H}^4\text{O}^2$	173	0.8937	0.9371	0.9666	959	1849	3647	19-52
$\text{NiO} \cdot \text{C}^4\text{H}^4\text{O}^2$	177	0.8943	0.9366	0.9653	963	1852	3646	25-56
$\text{ZnO} \cdot \text{C}^4\text{H}^4\text{O}^2$	183.4	0.9138	0.9538	0.9730	990	1892	3681	19-51
		5 Aq.	10 Aq.	25 Aq.	5 Aq.	10 Aq.	25 Aq.	
$\text{H}^2\text{O} \cdot \text{C}^4\text{H}^4\text{O}^2$	120	0.7320	0.8220	0.9157	153.7	246.6	522	21-52
$\text{K}^2\text{O} \cdot \text{C}^4\text{H}^4\text{O}^2$	196.3	—	0.6391	0.7728	—	240.5	499.4	20-51
$\text{PbO} \cdot \text{C}^4\text{H}^4\text{O}^2$	325	—	—	0.6824	—	—	529	18.51

$\text{ZnO} \cdot \text{C}^4\text{H}^4\text{O}^2 + 30 \text{ Aq.}$; sp. heat 0.8764; mol. heat 627. This solution remains supersaturated at ordinary temperatures, like that of lead acetate with 25 Aq. For the *monohydrate of acetic acid* were found, sp. heat 0.4932; mol. heat 59.2.

Carbonates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
$\text{K}^2\text{O} \cdot \text{CO}^2$	138.3	{ 0.8458 0.8509	{ 0.9104 0.9157	{ 0.9513 0.9543	{ 878 884	{ 1765 1775	{ 3556 3567	{ 22-27 21-52
$\text{Na}^2\text{O} \cdot \text{CO}^2$	106.1	{ 0.9037 0.9072	{ 0.9409 0.9435	{ 0.9675 0.9695	{ 909 913	{ 1793 1798	{ 3585 3593	{ 21-26 21-52
		10 Aq.	15 Aq.	25 Aq.	10 Aq.	15 Aq.	25 Aq.	
$\text{K}^2\text{O} \cdot \text{CO}^2$	138.3	0.6248	0.6831	0.7596	199	279	447	21-52
$\text{Na}^2\text{O} \cdot \text{CO}^2$	106.1	—	—	0.8649	—	—	481	21-52

Oxalates.

		50 Aq.	100 Aq.	200 Aq.	50 Aq.	100 Aq.	200 Aq.	
$\text{H}^2\text{O} \cdot \text{C}^2\text{O}^2$	90	0.9423	0.9653	0.9814	933	1824	3621	20-52
$\text{K}^2\text{O} \cdot \text{C}^2\text{O}^2$	166.3	0.8339	0.9083	0.9504	895	1786	3579	21-52

The following comparison shows in ten-millionth parts the increase of the specific heats of saline solutions between the ordinary temperature and about 30 degrees above.

Substances	50 Aq	100 Aq	200 Aq	Substances	50 Aq	100 Aq	200 Aq
K ² Cl ²	32	24	7	Ba(NO ³) ²	—	—	-10
Na ² Cl ²	19	23	27	Pb(NO ³) ²	- 7	- 3-	11
CaCl ²	0	20	- 4	Mg(NO ³) ²	16	12	- 9
SrCl ²	22	8	- 6	K ² SO ⁴	—	55	29
BaCl ²	6	11	6	Na ² SO ⁴	31	20	20
MgCl ²	58	-10	13	MgSO ⁴	36	5	3
K ² (NO ³) ²	15	23	45	CuSO ⁴	109	64	25
Na ² (NO ³) ²	20	0	31	Na ² (C ² H ³ O) ²	9	16	43
Ca(NO ³) ²	-8	- 6	1	Ca(C ² H ³ O ²) ²	45	30	- 7
Sr(NO ³) ²	"	- 2	- 8	Pb(C ² H ³ O ²) ²	1½	11	5
				Mean	21	16	11

So far as these numbers are within the limits of experimental error, it may be inferred from them that the specific heat of a saline solution increases for the most part with its temperature; and the mean values show that this increase is greater as the solution is more concentrated. It must be observed, however, that those numbers show, not the absolute increase of the specific heat, but only the amount by which this increase exceeds that of the specific heat of the water, inasmuch as Marignac's experiments give, in all cases, the specific heat of the solutions as compared with that of water between the same limits of temperature.

The observations above recorded show unmistakably a certain degree of parallelism between the several series of salts. The bases for the most part range themselves in the same series, although to this rule there are numerous exceptions. For the greater number of salts, the experiments show that the specific heat of a saline solution is much less than the sum of the specific heats of its constituents, that is to say the salt and the water. This, however, is by no means a universal rule, for most of the acetates exhibit the contrary relation, especially those of zinc, lead and nickel; solutions of acetic acid exhibit a similar departure from the rule.

Specific Heat of Mixed Saline Solutions.—The following experiments by Marignac show that the differences between the molecular heats of solutions of mixed salts, and those of their constituents, are very small, and do not exceed the limits of experimental error:

	Single Solutions		Sum	Mixed Solutions		
	Molecular Heat			Sp. Heat	Mol. Heat	Temp.
Na ² Cl ²	+ 50 Aq	893	1808	0·8810	1814	20°-50°
Na ² SO ⁴	50 Aq	915				
Na ² Cl ²	100 Aq	1783	3583	0·9300	3589	"
Na ² SO ⁴	100 Aq	1800				
K ² Cl ²	100 Aq	1760	3530	0·8994	3530	17-22
K ² SO ⁴	100 Aq	1770				
K ² Cl ²	200 Aq	3555	7115	0·9443	7104	"
K ² SO ⁴	200 Aq	3560				
Na ² Cl ²	50 Aq	893	1769	0·8560	1766	21-53
K ² Cl ²	50 Aq	876				
Na ² Cl ²	100 Aq	1783	3548	0·9187	3552	"
K ² Cl ²	100 Aq	1765				
Na ² Cl ²	200 Aq	3577	7135	0·9563	7140	"
K ² Cl ²	200 Aq	3558				
K ² SO ⁴	100 Aq	1770	3542	0·9096	3542	20-25
MgSO ⁴	100 Aq	1772				
K ² SO ⁴	200 Aq	3560	7112	0·9495	7116	"
MgSO ⁴	200 Aq	3550				
K ² SO ⁴	100 Aq	1770	7206	0·9344	7212	24-28
Al ² (SO ⁴) ³	300 Aq	5436				
K ² SO ⁴	200 Aq	3560				
Al ² (SO ⁴) ³	600 Aq	10833				
			14393	0·9667	14420	"

On the relations between the Specific Heat of Solutions and Liquid Mixtures and the quantities of heat evolved or absorbed in the act of dissolution or of mixture, see HEAT OF CHEMICAL COMBINATION (pp. 975-977, 980 and 993).

7. **Specific Heat of Gases.** The determination of the ratio, $\frac{c_p}{c_v} = k$, of the specific heat of gases at constant pressure to the specific heat at constant volume (iii. 40), has lately been made the subject of numerous investigations. The following results have been obtained by Röntgen (*Pogg. Ann.* cxviii. 580):

For air, $k = 1.4053$ Mean of 10 experiments in which the greatest deviations from the mean were $+0.0020$ and -0.0021 .
 „ CO_2 , $k = 1.3062$ Mean of 10 exp. Greatest deviations $+0.0020$ and -0.0028 .
 „ hydrogen, $k = 1.3852$ Mean of 8 exp. Greatest deviations $+0.0045$ and -0.0032 .

E. Wiedemann (*Ann. Phys. Chem.* [2], ii. 195-217) has investigated the specific heats of vapours and their alterations according to the temperature. In the following table c_0 denotes the specific heat at 0° under constant pressure, referred to the unit of weight; 2α the alteration produced by one degree of temperature. For comparison, the same magnitudes are given for the vapour of carbon disulphide, as determined by Regnault; also the specific heats of the corresponding liquids according to Regnault, and that of benzene according to Schüller (*Pogg. Ann.* Ergbd. v. 251):

	Vapour		Liquid	
	c_0	α	c_0	α
Chloroform	0.1341	0.0000677	0.23235	0.000050716
Carbon Disulphide	0.1315	0.0000963	0.23523	0.000081515
Ethyl Bromide	0.1354	0.0001780		
Ether	0.3725	0.0004268	0.52901	0.0002958
Acetone	0.2981	0.0003869	0.5064	0.0003965
Acetic Ether	0.2738	0.0004350	0.52741	0.0005232
Benzene	0.2237	0.0005114	0.37980	0.0007200

These numbers show that the greater the specific heat of any liquid at a given temperature, the greater also is that of its vapour. The variations in the specific heats of liquids and of the corresponding vapours, are of the same order of magnitude, and, in a series of instances, nearly equal to one another.

In the next table, n denotes the number of atoms contained in a molecule of the liquids named in the first column; d the density of the several vapours; c_0 the specific heat under constant pressure referred to the unit of weight; c_p and c_v the specific heats at constant pressure and constant volume referred to equal volumes (spec. heat of air = 1); $\frac{c_p}{c_v}$ the ratio of the two; $\frac{L}{H}$ the ratio of the energy, L , of the progressive motions to the total energy, H , contained in the gas; α' the magnitude α (preceding table) referred to the volume, its double value representing the alteration of the specific heat referred also to the volume:

	n	d	c_0	c_p	c_v	$\frac{c_p}{c_v}$	$\frac{L}{H}$	α'
Air	2	1	0.2389	1	0.7119	1.405	0.607	0.000
Hydrogen	2	0.0692	3.410	0.9877	0.6996	1.411	0.617	0.000
Carbon Monoxide	2	0.9674	0.2426	0.9822	0.6941	1.415	0.622	0.000
Carbon Dioxide	3	1.5290	0.1952	1.248	0.959	1.300	0.450	0.001389
Carbon Disulphide	3	2.6325	0.1315	1.448	1.160	1.248	0.372	0.001061
Nitrogen Monoxide	3	1.5250	0.1983	1.266	0.977	1.294	0.441	0.001461
Ammonia	4	0.5894	0.5009	2.236	0.947	1.303	0.464	0.007508
Chloroform	5	4.192	0.1342	2.358	2.070	1.139	0.208	0.001176
Ethylene	6	0.9674	0.3364	1.361	1.072	1.270	0.403	0.00334
Ethyl Bromide	8	3.7316	0.1354	2.106	1.818	1.159	0.237	0.002768
Acetone	10	2.0220	0.2984	2.468	2.180	1.132	0.198	0.003274
Benzene	12	2.6943	0.2237	2.523	2.235	1.129	0.184	0.004581
Ethyl Acetate	14	3.0400	0.2619	3.333	3.045	1.094	0.141	0.005537
Ethyl Oxide	15	2.5563	0.3725	3.934	3.696	1.078	0.116	0.004564

It is remarkable that the variation of the specific heat α' referred to the volume increases, for the most part, with the number of atoms in the molecule.

The difference between the specific heat of the same gas at constant pressure and at constant volume is due to the fact that when the gas is heated under constant pressure, and therefore allowed to expand, there is a certain amount of work employed in separating the particles of the gas, and a certain quantity of heat must be expended in performing this work, just as if the gas were confined in a cylinder with a movable piston which had to be raised; whereas, when the gas is heated under constant volume and therefore not allowed to expand, there is no such work to be done, and therefore all the heat applied is expended in raising the temperature of the gas, that is to say, in increasing the *vis viva* of its molecules. Now Clausius has calculated, on the principles of the mechanical theory of heat, that in a perfect gas the ratio of $c_p : c_v$ should have the value 1.67. But the numbers in the preceding table show that for all the ordinary gases and for many vapours, the ratio, as determined by experiment, is considerably less than this, varying from 1.405 for air to 1.078 for ethyl-vapour. Hence it may be inferred that when these gases, all of which are diatomic, are heated under constant volume, part of the heat is expended in performing, not external work, but a certain amount of work within the two-atom molecule. That this is the correct view is shown by the case of mercury-vapour, which is a monatomic gas, and in which, as appears from the recent experiments of Kundt and Warburg on the ratio between the lengths of the same wave of sound in air and in mercury-vapour (*Deut. Chem. Ges. Ber.* viii. 945), this interior work is not produced, and consequently the ratio $c_p : c_v$ is exactly that which is indicated by theory, viz. 1.67.

If similar experiments were made on the vapour of sulphur, which at temperatures not far removed from its boiling point, is hexatomic, and on those of phosphorus and arsenic, which are tetraatomic, it is probable that the ratio of the two specific heats would be found to be less than in the ordinary diatomic gases.

EXPANSION BY HEAT.

1. **Of Gases.** Andrews (*Proc. Roy. Soc.* xxiii. 514; xxiv. 455) infers from further experiments on the change of volume of carbon dioxide at different pressures and temperatures that, for the ordinary gaseous state, Gay-Lussac's law does not hold good either at constant pressure or at constant volume; but that the expansion by heat of a body in the ordinary gaseous state, whether it be measured by the increase of volume under constant pressure, or by the increase of elastic force under constant volume, is not a simple function of the initial volume or of the initial elastic force, but a complex function which changes with the temperature.

According to Mendelejeff and Kajander (*Deut. Chem. Ges. Ber.* viii. 1681), the expansion-coefficient of atmospheric air under a pressure of 750–770 mm. is $\alpha = 0.0036893$; in a subsequent communication (*Compt. rend.* lxxxii. 450), the same authors give for the expansion-coefficient under ordinary atmosphere pressure, $\alpha = 0.0036843$.

Troost and Hautefeuille (*Compt. rend.* lxxxiii. 333) have determined the compressibility and expansion-coefficients of certain vapours which can be mixed without entering into chemical combination. In the following table, the 'contraction' signifies the difference between the volume as found by observation, and that which it should be according to Boyle's law, when the pressure is increased from 0.5 to 1 atmosphere.

Vapour	B. P.	Contraction		Mean Expansion-coefficient	
		at 100°	at 180°	from 100° to 125°	from 125° to 180°
Silicon chloride	59°	2.07 per cent.	0.455 per cent.	0.00449	0.00399
Carbon tetrachloride	78.1°	1.38 „	1.367 „	0.00470	0.00414
Phosphorus trichloride	78°	„ „	1.548 „	0.00489	0.00417

Hence it appears that, for each of these vapours, the result of a density-determination at a given temperature must vary with the pressure, and at a given pressure with the temperature; and in calculating the elastic force of a mixture of two vapours, of known weight, volume, and temperature, from the sum of the elastic forces of the separate vapours, making use of the theoretical data applicable to these vapours under low pressure and high temperature, numbers are obtained, the sum of which exceeds the total pressure found by observation. This is a circumstance which requires to be taken into account in the determination of the densities of vapours mixed with air or nitrogen gas, as in Playfair and Wanklyn's experiments on the density of nitrogen tetroxide (iv. 76), and those of Wurtz on the vapour-density of phosphorus pentachloride (*Compt. rend.* lxxvi. 401).

Expansion of Mercury. A. Wüllner (*Pogg. Ann.* cliii. 440-447) has discussed the experiments of Regnault on the absolute expansion of mercury at different temperatures (iii. 56), and has calculated a new formula which represents the experimental results more exactly than that of Regnault, or than the formula deduced by Bosscha (*Pogg. Ann. Ergänzungsband*, v. 276). The mean coefficient of expansion of mercury for temperatures between 0° and 100°, calculated by Wüllner's formula, is somewhat greater than that given by Regnault's formula, and for lower temperatures (0°-30°) Wüllner's formula gives a value of the mean coefficient about 1 per cent. larger than that deduced from the formula of Regnault, thus:

	Wüllner	Regnault
0°-100°	0.00018253	0.00018153
0°-30°	0.00018153	0.00017976

A table of the results calculated according to the formulæ of Regnault, Bosscha, and Wüllner is given in the *Jahresb. f. Chem.* 1874, 70.

Expansion of Solids. Experiments on the expansion of metals and of woods have been made by P. Glatzel (*Ann. Chim. Phys.* clx. 497-514; *Chem. Soc. J.* 1877, ii. 820), with a new apparatus constructed by Fues of Berlin. The numbers in the following table give the increase of length, in millimeters, of bars 1 dem. long for a rise of 1°, so that if α denote the usual coefficient of expansion, i.e. in parts per million, these numbers must be denoted by 100 α . For comparison the numbers obtained by Fizeau by his optical method (1st *Suppl.* 675) are also given.

	Glatzel	Fizeau	
Steel	0.001256	0.001322	Different sorts.
		0.001101	
		0.001095	
Iron	0.001387	0.001210	"
		0.001188	
Copper	0.001705	0.001696	
Tin	0.002212	0.002234	
Aluminium	0.002354	0.002318	
Lead	0.002936	0.002924	
Cadmium	0.003121	0.003069	

In the determination of all these values by Glatzel, both the lengthening of the bar by heating, and its subsequent shortening by cooling down to the temperature of the air, were taken into account; and in this it was noticed, as previously found by other observers, that the bars on cooling did not assume exactly their original length, but became shorter.

For woods, the following values of 100 α were obtained in the direction of the fibres.

Maple	0.000502	Beech	0.000716
Hornbeam	0.000604	Pear	0.000721
Rosewood	0.000608	Oak	0.000746
Spruce fir	0.000608	Poplar	0.000761
Box	0.000623	Mahogany	0.000784
Elm	0.000635	Ash	0.000951
Alder	0.000699	Ebony	0.000970

The peculiarities above noticed in heating and cooling in the case of the metals were likewise observed in the woods.

The expansion of phosphorus has been investigated by Pisati and de Franchis (*Gazz. chim. ital.* 1874, 457). The specific gravities of solid and melted phosphorus at various temperatures were found to be as follows:—

	Solid		Fused
at 0°	1.83676	at 40°	1.74924
„ 20°	1.82321	„ 100°	1.69490
„ 44°	1.80681	„ 280°	1.52867

The volume-ratio between solid and liquid phosphorus was found to be 1.03446 at 40° and 1.0504 at 44°. For the latter temperature H. Kopp had previously found the value 1.0343 (*Liebigs Annalen*, xciii. 129). The volume of solid phosphorus at t° , referred to that at 0°, is given by the equation:

$$V_t = V_0 + 0.000200t + 0.000000115t^2;$$

the volume of liquid phosphorus between 50° and 280°, referred to that at 50°, by

$$V_t = V_{50} + 0.0002969(t-50) + 0.0000002115(t-50)^2.$$

The mean expansion-coefficient for solid phosphorus is

$$K = 0.0003674 + 0.000000211t.$$

that of liquid phosphorus at 50° and above, is

$$K = 0.0005167 + 0.000000370(t - 50).$$

The statement of Schrötter (*Liebig's Annalen*, lxxviii. 247) that melted phosphorus at 44° has a higher specific gravity than solid phosphorus at 10°, may be explained by the contraction which attends the partial conversion of ordinary into red phosphorus. In the experiments of Pisati a. de Franchis, this change was as far as possible prevented.

Sulphur.—Despretz found in 1838 that the expansion-coefficient of melted sulphur increases with tolerable regularity as the temperature rises (from 110° to 250°), H. Kopp (*Liebig's Annalen*, xciii. 129) found the expansion between 126° and 152° to be uniform, but different in amount from that given by Despretz. A new determination has been made by G. Pisati (*Gazz. chim. ital.* 1874, 29) by two methods, with the dilatometer and the weight-thermometer, the result of which is to show that at 150° the expansion is not quite uniform, but exhibits only very slight variations, and that between 150° and 160° a sudden and very considerable diminution in the rate of expansion takes place, whilst between 160° and 300° it increases, but so slowly, that even at 300° the rate still falls short of the value which it had at 150°. The mean coefficients determined by Pisati are about $\frac{1}{2}$ smaller than those of Despretz, and (between 126° and 152°) about $\frac{1}{20}$ larger than those given by Kopp. The coefficient of expansion diminishes from the melting point to about 170°, where it attains a minimum, and then exhibits a normal increase. Moitessier (*Jahresh. f. Chem.* 1866, 27) attributes these variations to the formation, during the heating, of the insoluble modification of sulphur, which has a smaller coefficient of expansion than soluble sulphur. The quantities of insoluble sulphur (in percentages of the total amount) formed at different temperatures were found to be as follows:

143°	148.5°	159.0°	167.4°	179.1°	213.5°	249.9°	284.9°	440°
0	2.54	7.03	14.77	22.60	27.09	26.31	29.31	30.27

According to these numbers, the effect of the less expansible insoluble sulphur in diminishing the expansion coefficient of the whole increases from 143° to about 200°, and then becomes nearly constant.

Pisati, by heating melted sulphur to 300°, and then cooling it to 125°, obtained a curve of expansion agreeing very nearly with that laid down from Moitessier's determinations.

According to Seichilone (*Gazz.* 1877, 501), sulphur, precipitated from sodium persulphide and purified by repeated crystallisation from carbon sulphide, gives, when gradually heated up to 440°, values of the coefficient of expansion agreeing with those obtained by Moitessier.

Ebonite. F. Kohlrausch (*Pogg. Ann. Ergänzbd. xi.* 314) finds that the expansion-coefficient of ebonite for 1° is—

$$0.0000770 \text{ between } 16.7^\circ \text{ and } 25.3^\circ$$

$$0.0000842 \quad \text{,,} \quad 25.3^\circ \quad \text{,,} \quad 35.4^\circ$$

$$\therefore \text{therefore } \alpha_t = 0.000061 + 0.00000076t.$$

These numbers show that both the expansion of ebonite, and the rate of its increase with rise of temperature, are very considerable. In this respect ebonite presents a marked contrast to soft caoutchouc, the difference being probably due to the sulphur in the ebonite. A rod of ebonite about 1 cm. thick was found, when heated, to take a considerable time to contract to a constant length—an effect which is attributed by Kohlrausch, not only to the bad conduction of the material, but to the fact that expansion by heat, like elastic alteration of form, does not take place instantaneously, but goes on with gradually diminishing rapidity after the alteration of temperature has taken place, as indeed is indicated by Matthiessen's experiments on glass rods (*Proc. Roy. Soc.* xiv. 551).

FUSION AND SOLIDIFICATION.

The softening and melting points of **metallic alloys** have been determined by R. Gnehm (*Monit. scient.* [3], iv. 424) by the following method:—Two rings of the alloy, free from oxide were fitted one into the other, and suspended by a hooked iron wire in a heated bath of oil or paraffin; and the temperatures were noted at which the rings first became elongated into ellipses, then into a vertical strip, and finally melted. The following are the results:

Alloy		Softening point	Melting point
Tin	Lead		
2	5	185°	189°
2	6	189°	194° to 195°
2	7	192°	198°
2	8	202°	208° to 210°

Melting Points of Fat and Wax. C. H. Wolff (*Dingl. pol. J.* cexvii. 411) has determined the melting points of the following kinds of fat and wax, by a modification of the method described by Löwe (*Dingl. pol. J.* cci. 250; *Chem. Soc. J.* 1871, 973).

	m. p.		m. p.
Ceresin	71·35°	Paraffin	49·5°
Yellow wax	64·0°	Spermaceti	45·2°
White wax	62·8°	Mutton suet	45·6°
Yellow wax in cakes *	60·1°	Japan wax	41·3°
Stearin	51·45°	Cacao butter	31·8°

Melting Points of Homologous Compounds. The following regularities in the melting points of homologous compounds have been observed by A. Baeyer (*Deut. Chem. Ges. Ber.* 1877, 1286). Both in the oxalic series and in the series of normal fatty acids, a member having an uneven number of carbon-atoms has, without exception, a lower melting point than the acid which contains one more carbon-atom. In the oxalic series of acids, the melting point of the acids with uneven numbers of carbon-atoms rises with increasing quantity of carbon, whereas that of the acids with even numbers of carbon-atoms falls, so that the two series meet at a certain intermediate point. In the fatty acid series, the melting points rise both in the even and in the uneven series, with exception of the lowest members. This is seen from the following table, taken from Fittig's *Lehrbuch*:

Melting Points of the Acids of the Oxalic Series.

Normal Succinic, $C^4H^4O^4$	180°	Normal Pyrotartaric, $C^5H^4O^4$. .	97°
Adipic, $C^6H^{10}O^4$	148°	α -Pinelic, $C^7H^{12}O^4$	102°
Suberic, $C^8H^{14}O^4$	140°	Azelaic, $C^9H^{16}O^4$	106°
Sebac, $C^{10}H^{18}O^4$	127°	Brassylic, $C^{11}H^{20}O^4$	108°

Melting Points of the Normal Fatty Acids.

Acetic, $C^2H^4O^2$	+ 17°	Propionic, $C^3H^6O^2$, remains fluid	
Butyric, $C^4H^8O^2$	0°	Valeric, $C^5H^{10}O^2$, "	"
Caproic, $C^6H^{12}O^2$	- 2°	Oenanthylic, $C^7H^{14}O^2$ "	- 10·5°
Caprylic, $C^8H^{16}O^2$	+ 16°	Pelargonic, $C^9H^{18}O^2$	+ 12°
Capric, $C^{10}H^{20}O^2$	+ 30°	—	
Palmitic, $C^{16}H^{32}O^2$	+ 62°	Margaric, $C^{17}H^{34}O^2$	+ 59·9°
Stearic, $C^{18}H^{36}O^2$	+ 69·2°	—	

Melting Points of Metallic Salts. T. Carnelley (*Chem. Soc. J.* 1876, i. 489–509; 1877, i. 365–388; 1878, *Transactions*, 273–281) has determined the melting points of a large number of metallic salts by the two following methods:

1. *The Specific Heat Method.*—The principle of this method is as follows: When a small quantity of the salt is placed in a weighed platinum crucible, and the latter is suspended in the flame of a Bunsen's burner or of a blowpipe, the temperature of the crucible after a time reaches that at which the salt fuses, if the latter is not beyond a certain limit; and now if the crucible, the instant the salt is seen to melt, be dropped

* Probably mixed with Japan wax.

into a known weight of water, of known temperature, and the rise in temperature noted, then, from the well-known equation for specific heats (iii. 27), we obtain the initial temperature of the crucible at the moment the salt melted, and therefore the temperature at which the fusion occurred, assuming that the mean temperature of the crucible is the same as that of the salt at the moment of melting. (For description and figures of apparatus, see the first paper above cited.)

Solidifying points may be determined in a similar manner, but with this difference, that when the salt has completely melted, the lamp is turned out, and the crucible while still suspended is carefully watched, and at the moment when the salt begins to solidify, dropt at once into the calorimeter, after which the process is the same as before. The point of solidification may usually be seen without difficulty, but sometimes the solidified salt forms a perfectly transparent glass, in which case it is very difficult, if not impossible, to tell when the salt becomes solid. In that case it is best, to place a bright gas flame at the opposite side of the crucible, so that its image may be seen reflected from the surface of the melted salt, which image, the moment the salt solidifies, becomes blurred and indistinct, or disappears altogether.

The following table exhibits the melting and solidifying points of several salts determined by this method and the differences between them :

	M. p.	S. p.	Difference
KNO ₃	353°	332°	21°
KClO ₃	372°	351°	21°
KCl	434°	415°	19°
KI	639°	622°	17°
KBr	703°	685°	18°
K ² CO ₃	838°	832°	6°

2. *The Time-method.*—This method depends upon the following principle: If three metallic salts, A, B, and C, which fuse at different temperatures, such that A fuses before B, and B before C, be arranged on a cold block of smooth iron, and this be placed in a muffle kept at a constant high temperature, and if x be the number of seconds which elapse between the melting of A and B, and y the number of seconds between the melting of A and C, then the ratio $\frac{y}{x}$ is approximately constant for the

same three salts, whatever may be temperature of the muffle, provided only it is considerably higher than that at which C fuses. This principle affords the means of determining the melting point of a refractory metallic salt by comparison with salts whose melting points have been determined by other methods. The following table shows the mean results of comparative experiments made by this method and by the specific heat method.

Salt	HgCl ^a	NaNO ^a	AgBr	TlI	AgCl	AgI	NaI	CaBr ^a	Li ² CO ^a	KBr	NaBr	CaCl ^a	NaCl
Time method	320	345	453	472	490	591	664	707	699	733	731	745	815
Specific heat method	315	345	453	466	477	554	661	710	729	733	742	753	811
Difference	+5	0	0	+6	+13	+37	-7	-3	-30	0	-11	-8	+4

Of the two methods, Carnelley considers the one depending on specific heats to be the more accurate, since the results obtained by it for the same salt agree more nearly among themselves than do those arrived at by the time method, while the exact point at which the salt melts is more easily seen in the case of the former. It has, moreover, the advantage of being entirely independent of any fixed melting points; whereas, in the time method, the melting points of the standard salts, as found by the other method, have to be assumed, so that the results which it yields are not wholly independent.

The specific heat method is, however, liable to an error arising from the overheating of the wire which suspends the crucible, and tending to make the results too high. This error may be reduced to a minimum by using a very thin suspending wire. The following table gives the melting points of a considerable number of salts determined with attention to this precaution. The new determinations relating to the salts previously examined are all lower than those given in the two preceding tables, partly from the cause just mentioned, and partly in consequence of a more exact determina-

tion of the heat-value of the calorimeter used in the experiments. For comparison, the melting points of some of the salts, as determined in the ordinary way with the mercurial thermometer (corrected, when not otherwise stated), or by other methods, are given in foot-notes. The values determined by the specific heat method are the means of several observations:

Salt	M. p.	Salt	M. p.	Salt	M. p.
(1) AsI^3	146°	SrI^2	507°	$(\text{PbVO}^3)^2\text{PbO}$	731°
(2) H^3BO^3	186	CdI^2	520	(21) KCl	734
(3) AgNO^3	217	(17) AgI	527	ZnF^2	734
(4) $\text{C}^2\text{H}^2\text{O}^1$	203	CdCl^2	541	(22) RbF	753
(5) HgBr^2	242	LiBr	547	(23) MoO^3	759
(6) LiNO^3	267	$\text{Cu(NO}^3)^2$	561	(24) NaCl	772
(7) Ti^2CO^3	273	$\text{Na}^2\text{B}^4\text{O}^7$	561	KF	789
(8) HgCl^2	293	NaVO^3	562	(25) $\text{Pb(PO}^3)^2$	800
(9) SbF^3	292	$\text{Na}^{12}\text{V}^8\text{O}^{26}$	562	(26) LiF	801
(10) NaClO^3	302	Ti^2VO^4	566	(27) $\text{P}^4\text{P}^2\text{O}^7$	806
(9) NaNO^3	316	CdBr^2	571	BaBr^2	812
(10) KNO^3	339	$\text{Ba(NO}^3)^2$	593	(28) Na^2CO^3	814
(11) KClO^3	359	(18) B^2O^3	577	Li^2SO^4	818
PbI^2	383	$(\text{NaVO}^3)^2\text{V}^2\text{O}^5$	581	(29) SrCl^2	825
$\text{Ag}^4\text{V}^2\text{O}^7$	383	(19) $\text{Ag}^4\text{P}^2\text{O}^7$	585	(30) K^2CO^3	834
$\text{Ag}^{12}\text{V}^8\text{O}^{26}$	384	LiCl	598	(31) Na^2SO^4	861
$\text{Ti}^{12}\text{V}^8\text{O}^{26}$	392	Cu^2I^2	601	(32) $\text{Pb}^3(\text{VO}^3)^3\text{Cl}$	a 802
ZnBr^2	394	NaPO^3	617	$\text{Pb(VO}^3)^4$	a 849
CaI^2	404	NaI	628	Ag^3PO^4	a 819
$\text{Ti}^{12}\text{V}^{10}\text{O}^{31}$	404	SrBr^2	630	Li^3PO^4	a 857
(12) $\text{Hg}^2\text{I}^2\text{Br}^2$	a 405	CaI^2	631	$\text{Ba}^2\text{V}^2\text{O}^7$	a 863
$\text{Ti}^{12}\text{V}^{14}\text{O}^{41}$	408	Ti^2SO^4	632	Na^3VO^4	a 866
$\text{Ba(ClO}^3)^2$	414	(20) KI	634	$\text{Na}^4\text{P}^2\text{O}^7$	a 888
TiVO^3	424	$\text{Ca(VO}^3)^2\text{V}^2\text{O}^5$	637	NaF	a 902
AgBr	427	RbI	642	CaF^2	a 902
(13) TiCl	427	$\text{Sr(NO}^3)^2$	645	SrI^2	a 902
(14) Ag^3VO^4	403°-565°	$\text{Na}^4\text{V}^2\text{O}^7$	654	BaF^2	a 908
Cu^2Cl^2	434	Ag^2SO^4	654	Cu^2F^2	a 908
TiI	439	V^2O^5	658	MgF^2	a 908
LiI	446	CaBr^2	670	BiI^3	decom- poses
ZnI^2	446	RbBr	683	BiF^3	did not melt at 804°, pro- bably de- composed
AgCl	451	Li^2CO^3	695		
$\text{Ti}^4\text{V}^2\text{O}^7$	454	MgBr^2	695		
TiBr	458	KBr	699		
(15) AgPO^3	482	NaBr	708		
CuCl^2	498	MgCl^2	708		
(16) PbCl^2	498	RbCl	710		
PbBr^2	499	CaCl^2	719		

The letter *a* before a number denotes that the salt referred to melts above that temperature.

(1) 146 (Carnelley); determined by thermometer.

(7) 184 (Carnelley).

(2) 219 (this Dictionary, iv. 104); 198 (Pohl, *Jahresb.* 4, 59; not stated whether correct or not. Determined by covering the bulb of a thermometer with a layer of fused salt, and then placing in an empty tube and heating); 218°, resolidifies at 212° (Carnelley).

(3) 200 (Carnelley). Anhydrous oxalic acid.

(5) 223 (Oppenheim, *Clarke's Constants of Nature*, but reference there given incorrect); 244 (Williams); 244 (Carnelley).

(6) 264 (Carnelley).

(7) 269 (Williams); 272 (Carnelley).

(8) 287 (Williams); 288 (Carnelley).

(9) 314 (Braun, *Pogg. Ann.* 154, 190); 310 (Person, *Ann. Chim. Phys.* 1847, xxi. 329); resolidifies at 313 (Schaffgotsch, *Pogg. Ann.* cli. 293); 319 (Carnelley).

(10) 342 (Braun, *Pogg. Ann.* cli. 190; 339 (Person, *Ann. Chim. Phys.* xxi. 329); resolidifies at 338 (Schaffgotsch, *Pogg. Ann.* cli. 293).

(11) 334 (Pohl, *Jahresb.* iv. 59), *vide* under AgNO^3 . It cannot be correct, since KClO^3 melts above KNO^3 . It is not stated whether 334° is the corrected temperature or not; if not the correction would make it several degrees higher.

(12) Did not melt but volatilised. The temperature given represents that at which all the salt had volatilised without melting. It therefore melts above 406.

(13) Above 260 (Crookes, *Chem. Soc. J.* 1864, 139).

(14) Very difficult to see when it melted. Appeared to soften and melt gradually.

(16) Prepared by precipitating AgNO^3 with an excess of NaPO^3 , the latter being obtained by fusing

In the case of some of the salts mentioned in the above table, it was impossible to determine the melting point in the ordinary way, as they decomposed into metallic oxide and free acid, owing to the presence of moisture in the air and from combustion of the lamp flame. The method adopted, therefore, was to heat the salt in question with two or three others of known melting point on a sheet of platinum, and observe between which two it melted. By this means the salt did not appear to decompose till after fusion, the melting point being reached much sooner than when the large platinum crucible was used.

VAPORISATION.

Boiling Points. A simple apparatus for the exact determination of boiling points is described by Berthelot (*Ann. Chim. Phys.* [5], xii. 562). It consists of a long-necked glass flask, having a capacity of 100–200 c.c. The neck is enclosed in a wide glass tube, closed with two perforated corks, and passes through the lower cork; and the tube of a thermometer passes through both, while its bulb is wholly immersed in the vapour. The lower cork is also traversed by a bent tube, which serves to carry off the vapour to a condenser, and thus prevent any excess of pressure in the apparatus.

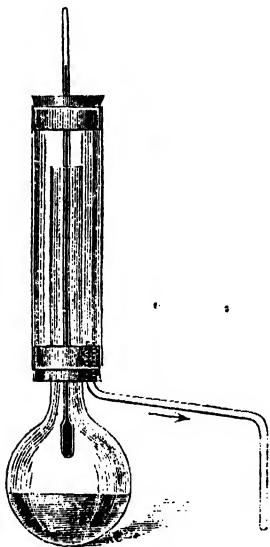


FIG. 3.

Another apparatus for the determination of boiling points under the normal barometric pressure is described by H. Bunte (*Liebig's Annalen*, clxviii. 139); and an apparatus for determining boiling points at all pressures below that of the atmosphere is described by Lothar Meyer (*ibid.* clxv. 303). The air is pumped out of the distillatory apparatus by means of a Bunsen's pump, and this apparatus is connected with a second distillatory apparatus and pump, in such a manner that the action of the pump stops as soon as the desired pressure is attained, but begins again as soon as any alteration of pressure takes place.

Determination of Boiling Points with small quantities of Substance.—A method for this purpose is described by H. Chapman Jones (*Chem. Soc. Jour.* 1878, xxxiii. 175), founded on the principle—previously applied to the determination of boiling points by Regnault—that the boil-

ing point of a substance is the temperature at which the tension of its saturated vapour is equal to the standard atmospheric pressure. A piece of glass tube, 4 mm. internal diameter and 200 mm. long, is bent in the form of a U, so that one end, which is open, extends at least 15 mm. beyond the other, which is closed. The bend is made in the form of a circle about 20 mm. in diameter. The liquid, two or three drops of which suffice for the determination, is introduced—by a method described at length in the paper above cited—into the closed end of the U-tube; the open end is placed

microcosmic salt. Became black on heating; fused mass, after cooling in water, was yellow, probably from conversion into Ag^+PO_4 .

(¹¹) 580 (Braun, *Pogg. Ann.* cliv. 190).

(¹²) 450 (Hodwell, *Chem. News*, xxxi. 4). This was simply deduced from the fact that it melted somewhat above the melting point of zinc, 412.

(¹³) Difficult to see, as it appeared to soften and then melt.

(¹⁴) Became black on heating; fused mass, after cooling in water, was yellow, probably due to formation of Ag^+PO_4 .

(¹⁵) 666 (Braun, *Pogg. Ann.* cliv. 190).

(¹⁶) 730 (Braun, *Pogg. Ann.* cliv. 190).

(¹⁷) Very deliquescent. Melting point very difficult to see.

(¹⁸) White; became very dark on heating (dark-green?), then whitish-yellow.

(¹⁹) 960 (Braun, *Pogg. Ann.* cliv. 190).

(²⁰) Becomes dark grey on heating, and white again at a red heat.

(²¹) The melting point was very difficult to see.

(²²) Undergoes some change on heating, as $\text{Pb}(\text{PO}_3)_2$.

(²³) 920 (Braun, *Pogg. Ann.* cliv. 190).

(²⁴) 910 (Braun, *Pogg. Ann.* cliv. 190).

(²⁵) 1150 (Braun, *Pogg. Ann.* cliv. 190).

(²⁶) 1280 (Braun, *Pogg. Ann.* cliv. 190).

(²⁷) Artificial vanadinite.

underneath the surface of some mercury contained in a small porcelain crucible. The whole is then slung by means of copper wire into a water or paraffin bath, and the temperature of the bath is gradually raised. The liquid will of course boil and the vapour will drive the air before it. On cooling, the whole tube—called a *tension-tube*—is filled with mercury, a bubble of liquid occupying the top of the bend. The tube is then inverted and the liquid transferred to the closed end of the tube. Any water or paraffin is now removed from the tube, and some mercury emptied from the open limb. The method of determining the boiling point is as follows:—The tube is immersed in a paraffin bath, care being taken that the open end is freely exposed to the air. The temperature is then gradually raised, and as the temperature approaches the boiling point of the substance, the mercury falls in the closed limb, the tube being gently tapped. At the moment the mercury levels in the two limbs are equal, the temperature of the bath is taken by a delicate thermometer placed close to the liquid in the closed limb. The bath is allowed to cool, and the temperature at which the levels pass each other again noted; and in this manner six observations are made, the mean of which gives the uncorrected boiling point.

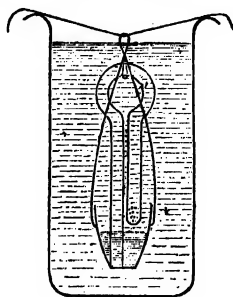


FIG. 4.

As an example of the determination by this method of the boiling point of a liquid under different pressures, the numbers obtained with carbon disulphide—usually said to boil at 46.6° under ordinary pressure, may be cited:

Pressure in mm.	736.0	744.5	752.0	762.0
B. p. at these pressures	45.1°	45.5°	46.0°	46.3°
B. p. at 760 mm.	46.0°	46.1°	46.3°	46.2°

By using a spermaceti bath, boiling points up to 300° may be determined.

Another apparatus for the same purpose is described by P. T. Main (*Chem. News*, xxxv. 59). It consists of two principal parts—a boiler-tube and a pressure-tube. The boiler-tube is a thin, narrow, glass tube, V-shaped, hermetically sealed at its short end, and open at the long end; the short end may be about 2 inches in length, the long end about 18 inches. The pressure-tube is a vertical glass tube, which can be connected with the open limb of the boiler-tube by a drying-tube, and dips into water contained in a wider glass tube: by raising or lowering this wider tube, the pressure within the open limb of the boiler-tube may be made greater or less than the atmospheric pressure. The boiler-tube is held so that the bend of it is its lowest point: in this position the liquid to be operated on is distilled or poured into it in such quantity that on inclining the tube, the air in the closed limb may be displaced by the liquid, which may be made to occupy the whole of this limb and a small portion of the open limb. By boiling this portion of liquid in the tube sufficiently, all dissolved air or gases may in general be expelled from the liquid, the space above which in the closed limb is then occupied by the vapour of the liquid only. The boiling point of the liquid must be known or determined first approximately, which is easily done by a preliminary experiment; and it may then be determined accurately (if less than that of water) by immersing the boiler-tube in water at a temperature a little higher than the boiling point of the liquid, connecting it with the pressure-tube, and increasing or diminishing the pressure by means of this so as to make it exactly equal to that of 760 mm. of mercury at 0° . By carefully lowering the temperature of the water till the liquid in the boiler-tube stands at exactly the same level in both limbs, and taking a few observations of the temperature while the liquid is steady in the boiler-tube, or oscillating slowly about this mean position, it is possible to determine the boiling point at 760 m.m., with considerable accuracy, with so little as 1 c.c. of liquid.

For liquids whose boiling points are higher than that of water the process would necessitate the use of dense aqueous solutions, or of some other liquid which can be heated to higher temperatures than water without boiling or decomposing.

High Boiling Points.—A method for the approximate estimation of the boiling points of substances which boil above the range of the mercurial thermometer is given by Carnelley and Carleton-Williams (*Chem. Soc. J.* [1878], xxxiii. 281). It consists in noticing whether certain salts melt on exposure to the vapour of the boiling substances, the melting points of the salts determined by Carnelley (pp. 936–938) being utilised for the purpose.

For temperatures below 500° the substance may be boiled in an ordinary distilla-

tion flask, provided with a perforated cork, through which pass several capillary tubes containing salts which melt at known temperatures. Substances which boil above 500° must be heated in a tube of hard glass by means of the blowpipe. The tube is held in a slanting position, and passes through a hole in the centre of a piece of sheet iron, in order to protect that portion which is above the boiling liquid from the action of the flame. The capillary tubes containing the salts must also be made of hard glass. When the vapour of the boiling substance attacks glass, it is often difficult to observe whether the salts have melted. In this case it is advisable to protect the tubes from corrosion by inclosing them in thin glass sheaths.

In the following table the boiling points determined by this method (Column III) are compared with the actual temperature (Column IV) measured by a mercurial thermometer, the stem of which was completely immersed in the vapour of the boiling liquid. Column I contains the formulæ of the substances, and II the salts used in determining the boiling point. The symbol + is used to indicate that the salt melts, and - to show that no change takes place.

I	II	III	IV	Remarks
HgCl ² . . . {	+ NaClO ³ - NaNO ³	{ 302°-316°	303° {	In this Dictionary (iii. 897) the b. p. given is 295°.
HgBr ² . . . {	+ NaNO ³ - KNO ³	{ 316°-339°	319° {	
SbCl ³ . . . {	+ AgNO ³ - HgI ²	{ 218°-241°	221° {	According to Kopp, 223°. Capitaine, 230°.
Diphenyl . . {	+ HgBr ² - Ti ² CO ³	{ 244°-278°	257° {	
Benzoic acid, m.-p. 121° {	+ HgBr ² - Ti ² CO ³	{ 244°-278°	249° {	Kopp (<i>Jahresb.</i> viii.), m. p. 121.4; b. p. 249.2.

Now on referring to the list of melting points previously mentioned, it will be seen that but few of the salts melt below 300° ; for these temperatures, therefore, the boiling point cannot be brought within such narrow limits as for higher temperatures. It must also be remembered that the method is meant to be used only for temperatures for which a mercurial thermometer cannot be employed, and in cases where merely an approximate knowledge of the temperature is required. The accuracy can obviously be increased by determining the melting points of a larger number of salts.

The following numbers show that good results are obtained at high temperatures:—

I	II	III	Remarks
Hg. . . . {	+ NaNO ³ + KNO ³ - KClO ³	{ 339-359°	The boiling point of Hg has been carefully determined by Regnault (<i>Jahresb.</i> xvi. 70) and by Dulong and Petit. The former found it to be 357.25°, and the latter 360°. Regnault (<i>Relation des Expériences, &c.</i> , ii. 527) states the b. p. of sulphur to be 447°. Hit- torf gives the same number, but according to Dumas, sulphur boils at 440°. Most of the determinations of the boiling points of S and Hg appear to have been made by means of the iodine pyrometer.
Sulphur purified by recrystallisation from carbon disulphide . . {	+ TlI + ZnI ² - AgCl	{ 446-451	

The method has been successfully applied in fractionating high-boiling hydrocarbons, and in determining the boiling points of the following substances :—

I	II	III	Remarks
Anthracene, the specimen melts at 212.5° ?	+ KNO_3 - KClO_3	339-359°	Græbe and Liebermann (<i>Lieb. Ann.</i> , Supp. vii. 264) state that anthracene boils a little above 360°, but they do not describe how they measured the temperature.
HgI^2	+ NaNO_3 + KNO_3 - KClO_3	339-359	Prepared by triturating iodine and mercury in presence of a small quantity of alcohol.
AsI^3	+ ZnBr^2 - $\text{Ba}(\text{ClO}_3)^2$	394-414	Prepared by subliming a mixture of As and iodine.
BiCl^3	+ $\text{Ba}(\text{ClO}_3)^2$ + TiCl - TiH	427-439	Two specimens, one prepared by dissolving bismuth in aqua regia, the other by burning the metal in chlorine, gave the same results. The chloride decomposes slowly on long continued boiling; chlorine is evolved, and golden needle-shaped crystals are deposited.
BiBr^3	+ AgCl + $\text{Ti}^{\text{IV}}\text{O}^7$ + AgPO^4 - PbCl^2 - AgI	454-498	Prepared by the action of bromine on the pure metal.
SbI^3	+ PbI^2 + $\text{Ba}(\text{ClO}_3)^2$ - TiCl - AgCl	417-427	Prepared by heating a mixture of iodine and antimony. The crude product was purified by sublimation over metallic antimony. The iodide melts at 171° (corr.), and decomposes slightly when boiled. The vapour has an intense dark red colour.
ZnBr^2	+ RbBr + Li^2CO^3 - KBr - NaBr	695-699	
PbCl^2	+ Na^2SO^4	Above 861	Prepared in the wet way; recrystallised from boiling water; attacks glass.
PbBr^2	—	—	Does not boil before the blowpipe. Attacks glass very rapidly.
CdCl^2	+ Na^2SO^4	Above 861	Two specimens gave the same results; a deposit separates out on boiling.

For the following substances a higher temperature is obtained by immersing the salts in the boiling liquid instead of in the vapour, whereas in the instances given above, the same result was obtained in both cases.

I	In vapour		In liquid		Remarks
	II	III t_b	IV	V	
ZnCl ²	$\left\{ \begin{array}{l} + V^2O^3 \\ + CaBr^2 \\ - RbBr \\ - KBr \end{array} \right.$	$\left\{ \begin{array}{l} 676-683^\circ \end{array} \right.$	$\left\{ \begin{array}{l} + KBr \\ + NaBr \\ - CaCl^2 \end{array} \right.$	$\left\{ \begin{array}{l} 708-719^\circ \end{array} \right.$	Attacks glass, and becomes turbid on boiling.
TiCl	$\left\{ \begin{array}{l} + Li^2CO^3 \\ + NaBr \\ - CaCl^2 \\ - KCl \end{array} \right.$	$\left\{ \begin{array}{l} 708-719 \end{array} \right.$	$\left\{ \begin{array}{l} + CaCl^2 \\ - 2(Pb^2V^2O^7)PbO \\ - KCl \end{array} \right.$	$\left\{ \begin{array}{l} 719-731 \end{array} \right.$	Melts to a pale yellow liquid, which changes to a cherry red, and finally again turns yellow.
TiH	$\left\{ \begin{array}{l} + NaCl \\ + Pb(PO^3)^2 \\ - Pb^2P^2O^7 \\ - Na^2CO^3 \end{array} \right.$	$\left\{ \begin{array}{l} 800-806 \end{array} \right.$	$\left\{ \begin{array}{l} + Pb^2P^2O^7 \\ - Na^2CO^3 \end{array} \right.$	$\left\{ \begin{array}{l} 806-814 \end{array} \right.$	Decomposes slightly on boiling.
Cd	$\left\{ \begin{array}{l} + KCl \\ + MoO^3 \\ - NaCl \\ - Na^2CO^3 \end{array} \right.$	$\left\{ \begin{array}{l} 763-772 \end{array} \right.$	$\left\{ \begin{array}{l} + MoO^3 \\ NaCl \text{ begins to melt.} \end{array} \right.$	$\left\{ \begin{array}{l} 772 \end{array} \right.$	Deville and Troost (<i>Compt. rend. xlix. 240</i>) give 860° as the boiling point of Cd, but how this number was obtained is not clearly stated.

Relation of Boiling Point to Chemical Constitution.—The differences of boiling point in metameric bodies are explained by A. Naumann (*Deut. Chem. Ges. Ber.* vii. 173; *Jahresb.* 1874, 15) as follows: A comparison of the properties of bodies in their different states of aggregation leads to the supposition that a liquid molecule is made up of a considerable number of gas-molecules, and that in the passage from the liquid to the gaseous state, the complex liquid molecule is split up into the simple gas-molecules. According to the laws of universal attraction, the gas-molecules which make up the liquid molecule will, under otherwise similar circumstances, offer a greater resistance to any force tending to separate them, in proportion as they are more closely aggregated; and therefore the closer the aggregation, the higher will be the boiling point of the liquid. The most easily comparable relations are found in metameric bodies, in which the elementary atoms are the same in number and in kind, but differently arranged, especially in those which contain but a small number of different elements—the hydrocarbons for example—and in which therefore the disturbing influence of the different qualities of the atoms is reduced to a minimum; or in certain oxygenated compounds, which, by their similarity of chemical character, appear to have their oxygen-atoms similarly united to the other elements. The arrangement of the atoms of the individual molecules in single chains admits of a closer packing of these molecules than that which they can assume when, in consequence of the presence of lateral chains, the grouping of the atoms approximates to the spherical form. The more therefore the grouping of the atoms deviates from the rectilinear and approaches to the spherical form, the less closely will the gas-molecules be grouped in the liquid molecule, and the lower will be the boiling point.

Pentanes, C ⁵ H ¹²	Normal Pentane, CH ³ .CH ² .CH ² .CH ² .CH ³	38°
	Isopentane, CH ³ .CH ² .CH $\begin{smallmatrix} \text{CH}^3 \\ \text{CH}^3 \end{smallmatrix}$	30°
	Tetramethyl-methane, $\begin{smallmatrix} \text{H}^3\text{C} \\ \text{H}^3\text{C} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}^3 \\ \text{CH}^3 \end{smallmatrix}$	9.5°
Hexanes, C ⁶ H ¹⁴	Normal Hexane, CH ³ .CH ² .CH ² .CH ² .CH ² .CH ³	70°
	Isohexane, CH ³ .CH $\begin{smallmatrix} \text{CH}^2\text{CH}^3 \\ \text{CH}^2\text{CH}^3 \end{smallmatrix}$	62°
	Di-isopropyl, $\begin{smallmatrix} \text{H}^3\text{C} \\ \text{H}^3\text{C} \end{smallmatrix} \text{CH}-\text{CH} \begin{smallmatrix} \text{CH}^3 \\ \text{CH}^3 \end{smallmatrix}$	58°
	Trimethyl-ethyl-methane, $\begin{smallmatrix} \text{H}^3\text{C} \\ \text{H}^3\text{C} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH}^2 \\ \text{CH}^3 \end{smallmatrix}$	43°-48°

Alcohols, $C^4H^{10}O$	Normal Butyl Alcohol, $CH^3.CH^2.CH^2.CH^2OH$	116°
	Isobutyl Alcohol, $\begin{matrix} H^3C \\ \\ H^2C \end{matrix} > CH.CH^2OH$	109°
	Secondary Butyl Alcohol, $CHOH < \begin{matrix} CH^3 \\ \\ CH^2-CH^3 \end{matrix}$	89°
	Tertiary Butyl Alcohol, $COH < \begin{matrix} CH^3 \\ \\ CH^3 \\ \\ CH^3 \end{matrix}$	82.5°
Acids, $C^5H^{10}O_2$	Normal Valeric Acid, $CH^3.CH^2.CH^2.CH^2.COOH$	185°
	Ordinary Valeric Acid, $\begin{matrix} H^3C \\ \\ H^2C \end{matrix} > CH-CH^2.COOH$	175°
	Trimethylacetic Acid, $(CH^3)_3C-COOH$	161°
Aldehydes, $C^5H^{10}O$	Normal Valeraldehyde, $CH^3.CH^2.CH^2.CH^2.CHO$	102°
	Ordinary Valeraldehyde, $(CH^3)_2CH-CH^2.CHO$	92°
Ketones, $C^5H^{10}O$	Methyl-propyl Ketone, $H^3C-CO-CH^2.CH^2.CH^3$	99°-105°
	Methyl-pseudopropyl Ketone, $H^3C-CO-CH(CH^3)_2$	93.5°

Influence exerted on the Boiling point of Oxygenated Carbon-compounds by the position of the Oxygen-atom.—This influence, likewise investigated by Naumann (*Ber. vii. 206; Jahresb. 1874, 17*), may be expressed as follows: In metameric bodies of similar chemical character and otherwise corresponding structure, the more nearly the oxygen stands to the middle of the chain of atoms, the lower will be the boiling point. The following may be taken as examples:—

Normal Alcohols	$C^4H^{10}O$	Primary Butyl Alcohol, $CH^3.CH^2.CH^2.CH^2OH$	116°
		Secondary " " $CH^3.CHOH.CH^2.CH^3$	99°
	$C^5H^{12}O$	Primary Pentyl Alcohol, $CH^3.CH^2.CH^2.CH^2.CH^2OH$	137°
		Methyl-propyl Carbinol, $CH^3.CHOH.CH^2.CH^2.CH^3$	120°-123°
Iso-alcohols	$C^6H^{14}O$	Primary Hexyl Alcohol, $CH^3(CH^2)_4CH^2OH$	150°-156.6°
		Methyl-butyl Carbinol, $CH^3.CHOH(CH^2)_3CH^3$	140°-142°
	$C^5H^{12}O$	Isopentyl Alcohol, $(CH^3)_2CH-CH^2-CH^2OH$	128°-132°
		Methyl-pseudopropyl Carbinol, $CH^3.CHOH.CH(CH^3)_2$	104°-108°
Mixed normal Ethers	$C^4H^{10}O$	Isopentyl Alcohol, $(CH^3)_2CH-CH^2-CH^2OH$	98.5°-100°
		Dimethyl-ethyl Carbinol, $CH^3.CH^2-COH < \begin{matrix} CH^3 \\ \\ CH^3 \end{matrix}$	
	$C^4H^{10}O$	Methyl-propyl Oxide, $CH^3.O.CH^2.CH^2.CH^3$	49°-52°
		Diethyl Oxide, $CH^3.CH^2.O.CH^2.CH^3$	-35.5°
Mixed iso-ethers	$C^5H^{12}O$	Ethyl-butyl Oxide, $CH^3.CH^2.O.CH^2.CH^2.CH^3$	-91.7°
		Dipropyl Oxide, $CH^3.CH^2.CH^2.O.CH^2.CH^2.CH^3$	85°-86°
	$C^6H^{14}O$	Methyl-isopentyl Oxide, $CH^3.O.CH^2.CH^2.CH(CH^3)_2$	92°
		Ethyl-isobutyl Oxide, $CH^3.CH^2.O.CH^2.CH(CH^3)_2$	78°-80°
Compound Ethers	$C^5H^{10}O_2$	Propyl Acetate, $CH^3.CO.O.CH^2.CH^2.CH^3$	101-98°
		Ethyl Propionate, $CH^3.CH^2.CO.O.CH^2.CH^3$	98-80°
	$C^6H^{12}O_2$	Butyl Acetate, $CH^3.CO.O.CH^2.CH^2.CH^2.CH^3$	124-30°
		Propyl Propionate, $CH^3.CH^2.CO.O.CH^2.CH^2.CH^3$	122-44°
		Ethyl Butyrate, $CH^3.CH^2.CH^2.CO.O.CH^2.CH^3$	121-07°
	$C^7H^{14}O_2$	Butyl Propionate, $CH^3.CH^2.CO.O.CH^2.CH^2.CH^2.CH^3$	145-99°
		Propyl Butyrate, $CH^3.CH^2.CH^2.CO.O.CH^2.CH^2.CH^3$	143-42°

The cause of this regularity appears to be that the more nearly the oxygen is placed to the middle of the chain, the more closely do the similar atoms of the several molecules approach one another—that is to say, the oxygen-atoms of the one to the oxygen-atoms of the other, and the carbon-atoms of the one to the carbon-atoms of the other. On the other hand, the position of the oxygen near the end of the chain leads to a more frequent approximation of the dissimilar atoms of the individual molecules, viz., the carbon-atoms of the one to the oxygen-atoms of the other; and this leads to the inference that the approximation of gas-molecules by their similar atoms does not bind them together into a liquid molecule so firmly as approximation by their dissimilar atoms.

Influence of Chlorination on the Boiling Points of Organic Compounds (L. Henry, *Ber. vi. 734*). The usual effect of the substitution of chlorine for hydrogen is to raise the boiling point. This takes place regularly and constantly in those derivatives in which the group CH^3 is associated with another positive hydrocarbon-group like CH^3 itself or C^2H^5 , &c., as in the chloro-derivatives of ethane and of toluene:

	Mol. wt.	B. p.		Mol. wt.	B. p.
$\text{CH}^3.\text{CH}^3$	30	Gas	$\text{C}^6\text{H}^5.\text{CH}^3$	92	111°
$\text{CH}^3.\text{CH}^2\text{Cl}$	64.5	10°	$\text{C}^6\text{H}^5.\text{CH}^2\text{Cl}$	126.5	176°
$\text{CH}^3.\text{CHCl}^2$	99	60°	$\text{C}^6\text{H}^5.\text{CHCl}^2$	161	208°
$\text{CH}^3.\text{CCl}^3$	133.5	75°	$\text{C}^6\text{H}^5.\text{CCl}^3$	195.5	214°

The presence of a negative group or radicle, on the other hand, produces in all the chlorine-derivatives—after the first—a very considerable diminution in the rise of the boiling point, as may be strikingly seen in the several chlorinated acids, amides, chlorides, aldehydes, &c., of the acetic series.

	B. p.	M. p.		B. p.
$\text{HOCO}.\text{CH}^3$	118°	17°	$(\text{C}^3\text{H}^3\text{O})\text{CO}.\text{CH}^3$	74°
" CH^2Cl	180°	62°	" CH^2Cl	143°
" CHCl^2	195°		" CHCl^2	156°
" CCl^3	195°-200°		" CCl^3	164°
$\text{HOCO}.\text{CH}^3$	118°		$\text{ClCO}.\text{CH}^3$	55°
" CH^2Br	208°		" CH^2Cl	105°
" CHBr^2	225°-230°		" CHCl^2	
" CBr^3	245°		" CCl^3	118°
$\text{H}^2\text{NCO}.\text{CH}^3$	221°	78°	$\text{HCO}.\text{CH}^3$	21°
" CH^2Cl	224°	116°	" CH^2Cl	
" CHCl^2	233°	96°	" CHCl^2	88°
" CCl^3	238°	136°	" CCl^3	96°
$\text{H}^3\text{C.CO}.\text{CH}^3$	56°			
" CH^2Cl	118°			
" CHCl^2	118°			

The boiling points of cyanogen-compounds are considerably lowered by the presence of a negative radicle, thus—

	B. p.
Hydrogen Cyanide, H.CN	26°
Cyanogen Chloride, Cl.CN	15°
Dicyanogen, CN.CN	21°
Propionitril, $\text{CH}^3.\text{CH}^2.\text{CN}$	96°
Acetyl Cyanide, $\text{CH}^3.\text{CO}.\text{CN}$	93°

On the contrary:

	B. p.
Propano, $\text{CH}^3.\text{CH}^2.\text{CH}^3$	Gas
Acetone, $\text{CH}^3.\text{CO}.\text{CH}^3$	55°

but again:

Ethylglycollic Nitril, $\text{C}^2\text{H}^3\text{O}.\text{CH}^2.\text{CN}$	154°-155°
Ethylecyanoformate, $\text{C}^2\text{H}^3\text{O}.\text{CO}.\text{CN}$	115°-116°

The monochloro-derivative of acetonitril boils at a much higher temperature than acetonitril itself, but the more highly chlorinated derivatives exhibit a considerable retrogradation in their boiling points, notwithstanding the gradual increase of their molecular weights:

	Mol. wt.	B. p.
$\text{CH}^3.\text{CN}$	41.0	81°-82°
$\text{CH}^2\text{Cl}.\text{CN}$	75.5	123°-124°
$\text{CHCl}^2.\text{CN}$	110.0	112°-113°
$\text{CCl}^3.\text{CN}$	144.5	83°-84°

In these compounds the methyl-group CH^3 , by conversion into CCl^3 , may be supposed to assume the functions of a negative radicle, and therefore to influence the boiling point in the manner above explained.

Relation between Boiling point and Vapour-density in Homologous Compounds.—According to F. Bunden (*Phil. Mag.* [4], xli. 528), the absolute boiling temperature of homologous hydrocarbons and ethers is proportional to the square-root of their vapour-density, as indicated by the formula:

$$T = 51.5 \sqrt{d} \text{ or } t = 51.5 \sqrt{d} - 273,$$

which was found to be true with regard to 71 bodies of the two classes just mentioned. For aldehydes, alcohols, and acids, on the other hand, the coefficient was not found to

be constant; and to isomeric bodies of equal molecular weight, but different boiling point, the law is clearly inapplicable.

Boiling of Saline Solutions.—C. G. Müller (*Deut. Chem. Ges. Ber.* ix. 1629) observes that saline solutions may be heated nearly to boiling by passing steam into them. Solutions of calcium chloride of various degrees of concentration, and boiling at 100° , 122.5° , 127° , and 150.5° , were brought, by the introduction of aqueous vapour at 100° , to the temperatures of 100° – 103° , 121.5° , 127° , and 147.5° respectively. Concentrated solutions of $\text{SO}^{\circ}\text{Na}^2$, NaCl , and $\text{NO}^{\circ}\text{K}$, boiling at 104.5° , 110° , and 114.5° , were raised by a current of steam to 104° , 109° , and 112.5° . An alcoholic solution of potassium acetate, boiling at 87° , was heated by alcohol vapour from 78.3° to 84° . When a thermometer, moistened with a solution of calcium chloride, is heated to 100° over a flame, and then brought into an atmosphere of aqueous vapour, it shows, not 100° , but the boiling temperature of the solution with which it is moistened, until all the salt is washed away. If a test-tube be filled to a third with water, moistened on the outside with solution of calcium chloride, heated to boiling over a flame, and then introduced into the vapour-space of a flask in which water is boiling, the water in the tube will be thrown into violent ebullition, lasting for about a minute, in consequence of the rise of temperature caused by the absorption of the steam by the calcium chloride. The temperature produced in a saline solution by the absorption of aqueous vapour is, however, always a little below the boiling point of the solution, in consequence of the cooling action of the vapour which is in excess: hence also a strong stream raises the temperature less than a weaker one.

The aqueous vapour given off from a boiling saline solution has, according to Müller, a temperature of only 100° , whereas, according to Magnus and Wüllner, its temperature is nearly the same as that of the solution itself. Müller considers that, if steam at 100° passed as above mentioned into a solution of calcium chloride, can raise its temperature to 147.5° , the vapour which forms within the boiling liquid may act in the same manner, and this view he regards as corroborated by the following facts: (1). The boiling of the liquid, that is to say, the tumefaction produced by the rising of vapour-bubbles to the surface and there bursting, begins below the maximum temperature, which is afterwards only gradually attained. A solution of calcium chloride, for example, having a maximum boiling point of 126° , begins to boil at 110° , and the temperature rises to 126° in about thirty seconds. (2). Saline solutions of high boiling point exhibit a higher temperature in gentle than in violent ebullition. The above-mentioned solution of calcium chloride showed a temperature of 126° when it boiled strongly, and of 127.5° when it boiled gently. If the flame be taken away from under the liquid while boiling violently, the thermometer is seen to rise 1 or 1.5 degrees. These effects may be explained by supposing that the vapour of water which rises through boiling saline solutions has a temperature of only 100° , and that the rise of temperature in the liquid is due to the absorption of a portion of it, while a rapid stream of vapour has a somewhat cooling effect. The bubbles of vapour which rise within the liquid act, in short, in the same manner as vapour introduced from without. Wüllner (*Ber.* x. 256) remarks that facts similar to those described by Müller as to the heating of saline solutions to their boiling points by the action of aqueous vapour at 100° were noticed more than fifty years ago by Faraday and by Gay-Lussac (*Ann. Chim. Phys.* 1822), and that the latter states, as the result of direct experiment, that the temperature of the vapour evolved from a liquid under any pressure whatever is always the same as that of the stratum of liquid in immediate contact with it. Pfaundler (*Ber.* t. 463) objects, on theoretical grounds, to the views put forward by Müller, who, on the other hand, still maintains, on the ground of the experiments above cited, and of others not yet published, that the bubbles of vapour which rise in saline solutions have, at the moment of their formation, a temperature of only 100° , and that the higher temperature which they may exhibit on emerging from the liquid is due to their becoming overheated by conduction, more or less according to the depth of the bath (*Ber.* x. 1327).

From observations on the boiling points of solutions of calcium chloride, H. Hammerl (*Wien. Akad. Ber.* [2 Abth.], lxxii. 8) deduces the interpolation equation:

$$t = 0.0519p + 0.011163p^2,$$

in which t denotes the excess of the boiling temperature above that of water, p the percentage of CaCl^2 in the solution:

p	t	
	Calc.	Obs.
14.3	3.0	2.7
28.6	10.6	10.9
41.5	21.3	20.5
51.9	32.8	31.8
58.4	40.5	40.3
64.6	50.1	51.2
70.8	59.8	62.4

whence also may be calculated the following more convenient form of table:

p . .	5	10	15	20	25	30	35	40	45	50	55	60	65	70
t . .	0.5	1.6	3.2	5.5	8.3	11.6	15.1	19.9	24.9	30.5	36.6	43.3	50.6	58.4

Boiling of Over-heated Liquids.—It is well known that a liquid heated in a vessel of glass or other material having a smooth surface may often be raised several degrees above its ordinary boiling point without actually boiling, and that the introduction of fragments of glass or other substances will then throw it into sudden and violent ebullition. Experiments on this subject have been made by Gernez (*Ann. Chim. Phys.* [5], iv. 335-401), from which he infers that solid bodies which determine the ebullition of over-heated liquids lose this property when they have previously been strongly heated; and those which do not act chemically on the liquids, no longer give rise to the formation of vapour bubbles after they have been used for some time to keep up the boiling. Bodies which have not been in contact with the air, and contain no air or gas in their interior, are without action on superheated liquids, but bodies which have been rendered inactive by the action of heat, or by prolonged immersion in a boiling liquid, recover their activity after exposure to the air; in fact, the boiling of superheated liquid is set up by contact with an atmosphere of gas. Gernez regards boiling as the evaporation of a liquid at the temperature of the normal boiling point towards the surfaces of gases, which are either introduced into the liquid from without, or developed within it in consequence of the heating of gas-solutions above the limit of supersaturation. An indefinitely small quantity of gas is sufficient to set up the boiling, which may then continue for any length of time, as each bubble of vapour which escapes leaves behind it a very small bubble capable of exciting further ebullition.

Critical observations on the experiments and conclusions of Gernez have been published by C. Tomlinson (*Phil. Mag.* [4], xlix. 432-448; l. 85-100).

Distillation of Liquids not miscible with Water in a current of Steam.—Experiments on this kind of distillation have been made by A. Naumann (*Ber.* x. 1421, 1819, 2014, 2099) on benzene, toluene, oil of turpentine, carbon tetrachloride, nitrobenzene, ethyl bromide, ethyl benzoate, and naphthalene, the first three of which are specifically lighter, the last five heavier than water. The boiler used for the lighter liquids was an upright tubulated receiver, into the lower part of which the steam was passed laterally in such a manner that, during the entire distillation, the orifice of the tube which conveyed the steam was never covered by the condensed water there collected, but was always immersed in the supernatant liquid, which formed a turbid mixture of water-drops with the other liquid. For the heavier liquids, in order to diminish the quantity required, a cylindrical tube, narrowing towards the bottom, was used. The mixture of liquids which distilled over was collected in graduated tubes; and after the water had been completely separated from the other liquid, the volumes of the two were measured, excepting in the case of naphthalene, in which the proportions were determined by weighing.

The following general laws were found to hold good for each of the eight fluid mixtures investigated: (1). A constant boiling point lower than that of the less volatile constituent. (2). A constant ratio of the constituents distilled over. (3). The ratio of the two constituents in the distillate, expressed in the known molecular weights deduced from the normal vapour-densities, is equal to the ratio of the vapour-tensions of the two constituents at the temperature of the mixed vapour. (4). The temperature of the mixed vapour is mostly above that of the liquid mixture.

These regularities are independent of the height of the space above the boiling mixture filled with the mixed vapours, but they presuppose that the layer of liquid

above the point where the vapour enters, shall not, in moderately rapid distillation, sink below 50 mm.

The following table shows the mean values deduced from numerous observations :

Substance	Molecular formula	Boiling point			Height of barometer (corr.) mm.	Ratio (in molecular weights) of the water to the substance in the distillate $\frac{g}{m} : \frac{G}{M}$	Ratio of the vapour-tension of the water to that of the other liquid at the temperature of the mixed vapour $p : P$
		Specific gravity	Of the substance alone (uncorr.)	Of the liquid mixture Temperature of the mixed vapour			
Benzene	C^6H^6	0.8773	79.5°	68.5° 69.1°	742	0.41	0.42
Toluene	C^7H^8	0.8657	108.5	82.4 84	752	1.27	1.26
Turpentine oil	$C^{10}H^{16}$	0.8827	160	93.2 94.8	745.5	6.6	5.83
Carbon Tetrachloride	CCl^4	1.599	76.1	65.7 66.7	747	0.36	0.36
Nitrobenzene	$C^6H^5N(O)^2$	1.2060	208	98.6 99	753	38.5	33.3
Ethyl Bromide	C^2H^5Br	1.4069	72	37 37	741	0.064	0.064
Ethyl Benzoate	$C^9H^8O^2$	1.048	213	98.7 99.1	751	49.91	45.99
Naphthalene	$C^{10}H^8$	—	218	97.4 98.8	750	38.98	36.4

From the law enunciated in (3), and established by the numbers in the last two columns of the preceding table, may be deduced a method of determining molecular weights by distillation or sublimation in indifferent vapours or gases. Let g denote the weight of one constituent of the distillate, m its molecular weight, and p its vapour-tension at the boiling temperature t of the mixture and the barometric pressure b ; also let G denote the weight of the other constituent of the distillate, M its molecular weight, and P its vapour-tension, likewise at the boiling temperature measured in the mixed vapour; then

$$\frac{g}{m} : \frac{G}{M} = p : P;$$

and if the molecular weight M be the quantity sought, we have

$$M = \frac{m G p}{g P}.$$

If one of the bodies is water, $m = 18$; p must be sought in Regnault's table of the tensions of water-vapour (iii. 93; also *Résumé des Expériences*, &c. p. 489); g and G are the relative weights in the distillate of water and the body under examination; and $P = b - p$. If a liquid or solid body which does not boil without decomposition, has at any temperatures a vapour-tension of only a few millimeters, there will most probably be found another body, boiling within these same temperatures, in which the body in question does not dissolve, and in whose vapour it can be volatilised, so that its molecular weight can then be determined in the manner above described. This method of determining molecular weights is likely to be especially useful in cases where the ordinary methods are inapplicable.

Evaporation. Experiments on the rate of evaporation of volatile liquids, such as ether and carbon sulphide, in open and in closed vessels have been made by J. Stefan (*Wien. Akad. Ber.* [2 Abth.], lxxiii. 388-423). The experiments were made with rather narrow tubes, in order to avoid as far as possible the great lowering of temperature consequent on rapid evaporation in shallow vessels. Experiments on evaporation from open tubes into the air led to the following conclusions. The rate of evaporation of a liquid from an open tube is inversely proportional to the distance between the level of the liquid and the open end of the tube, provided this distance exceeds about 10 mm. It is independent of the diameter of the tube (0.6 to

6 mm. in the experiments quoted). The rate is proportional to the logarithm of a fraction having for its numerator the atmospheric pressure, and for its denominator this pressure diminished by the maximum vapour-tension. For the case in which this tension is equal to the atmospheric pressure, the fraction representing the rate of evaporation becomes infinitely great, and the law then denotes another process, viz. ebullition. These laws may also be deduced from the theoretical discussion of the experiments founded on the mechanical theory of gases.

To study the rate of evaporation in closed tubes, a tube closed at one end was plunged by its open end into ether, whereupon bubbles were given off, somewhat quickly at first, afterwards more slowly, their rate of evolution being regulated by the following simple law: *The times in which equal numbers of successive bubbles are evolved follow the law of the uneven numbers, 1, 3, 5, &c.* If the tube contains hydrogen instead of air, the same number of bubbles is evolved in one-fourth of the time. As the number of bubbles gives a measure of the quantity of vapour formed, it follows, from the fact just stated, that ether evaporates in hydrogen gas four times as quickly as in air under similar circumstances. This result was confirmed by means of an apparatus in which a liquid could be left to evaporate in any given gas, under circumstances similar to those of evaporation in the open air, the ether being then found to evaporate in hydrogen 3.7 times as fast as in air.

When a tube provided with a stop-cock is dipped into ether with the cock open, and the cock is then closed, the level of the liquid within the tube sinks below the outer level, and the depths to which the inner level sinks in given times are proportional to the square roots of these times; or the quantity of vapour evolved in a given time is proportional to the square root of the time. This law agrees with that above stated as to the evolution of bubbles. Both laws, however, are true, not unconditionally for all times, but only for the beginning of the process. They may be regarded as exact until about half the quantity of vapour has entered the tube that is required for complete saturation. They are strictly true, as the theory of these experiments shows, for a tube of infinite length, and no deviation from them is perceptible so long as the partial pressure of the vapour which arrives at the closed end of the tube falls within the errors of observation. A theoretical investigation of the question shows that the evaporation of a liquid in a gaseous mixture leads to an alteration in the proportions of the constituents of that mixture, in consequence of which the more diffusible gas is found in the neighbourhood of the evaporating liquid in greater proportion to the less diffusible than in other parts of the space. If, therefore, a liquid be left to evaporate in a tube filled with detonating gas, the quantity of hydrogen in the neighbourhood of the liquid is relatively greater than in the other parts of the tube. Since now the nature of the gas in which a liquid evaporates has an essential influence on the rate of the evaporation, we ought in strictness, when discussing experiments on evaporation in the air, not to regard the air as a simple gas. But the difference between the behaviour of nitrogen and of oxygen is so small, that in diffusion-processes, the air may be regarded as a simple gas without sensible error.

Evaporation in Gases.—Experiments on the rate of evaporation in different gases have been made by W. Kirchman (*Arch. Pharm.* [3], ix. 423-427). Equal quantities of camphor were introduced into eight glass vessels, of the same size and shape, four being filled with air and the other four with carbon dioxide. After all the eight glasses had been exposed for some weeks to the same fluctuations of temperature, those filled with air were found to be covered with thick layers of camphor, while in those filled with carbon dioxide, the camphor remained at the bottom almost intact, the sides of these vessels being merely lined with a thin film of camphor crystals. Hence it appears that the volatilisation of the camphor is sensibly affected by the quality of the gas, just as the manner in which a solid body dissolves in a liquid is essentially affected by the nature of that liquid. Further experiments showed that carbon dioxide is also a relatively less favourable medium of evaporation than air for the terpenes, for chloroform and for carbon disulphide, but, on the contrary, a better medium for ethyl oxide, for methyl, ethyl, and amyl alcohols, and for water. Moreover, dry carbon dioxide was found to be an excellent medium for removing water from freshly distilled volatile oils. Air removes chlorine from chlorine-water even when not saturated; but the strongest chlorine-water is completely deprived of chlorine, by passing through it scarcely more than its own volume of carbon dioxide.

The following proportions between the rates of evaporation of liquids in different gases have been observed by G. Baumgartner (*Wien. Akad. Ber.* [2 Abth.], lxxv. 313, 689).

	In Air	In Carbon Dioxide	In Hydrogen	In Coal-gas
For Ether	1	0.80	3.33	1.50
„ Carbon Disulphide	1	0.61	3.35	1.60
„ Chloroform	1	0.64	3.65	1.69
„ Alcohol	1	—	3.58	1.80

Saturation of Air with Water-vapour, and Desiccation of Air.—From experiments by H. C. Dibbitts (*Zeitschr. anal. Chem.* 1876, 121, 170), it appears: (1). That air which has been dried by means of strong sulphuric acid becomes completely saturated with water-vapour by passing through water at a maximum rate of 30 litres per hour. (2). Air dried as described may be saturated with water-vapour by being caused to pass over the surface of water, provided that the surface of water exposed be not very small compared with the rapidity of the flow of air. (3). Concentrated sulphuric acid (containing not more than 8.4 per cent. water), dries air at temperatures up to about 25° so thoroughly that 100 litres do not give up to phosphoric anhydride more than 0.0002 gram. (4). If the temperature be higher than 25° or 30°, sulphuric acid does not desiccate air so completely; yet the quantity of water-vapour contained in 1 litre of air dried by means of sulphuric acid at 50° amounted to less than 0.0001 gram.

Phosphoric anhydride may be said to effect an almost absolute desiccation of air, the quantity of aqueous vapour left by it in a litre of air not exceeding an extremely small fraction of a milligram.

The desiccating power of calcium chloride is much affected by temperature. If air dried by passing over this salt at a given temperature be brought into contact with a fresh quantity of the same salt at a lower temperature, a further desiccation takes place; but if the second portion of calcium chloride be maintained at a higher temperature than the first, the air becomes moister. By passing a gas, already dried over calcium chloride, through a system of tubes containing equal weights of calcium chloride, positive or negative alterations in weight may be obtained, according as the different parts of the system possess a higher or lower temperature. If the temperature at the beginning of the system of tubes be the same as that at the end, the algebraic sum of the weight-alterations is always = 0; if these two temperatures differ, the system suffers a positive or negative weight-alteration, in proportion to the difference of temperature between the first and last tubes.

The following table of the weights of water-vapour contained in 1 litre of saturated air is calculated from the vapour-tension determinations of Regnault and of Magnus:—

Weight of water-vapour in milligrams			Weight of water-vapour in milligrams		
Temperature	Magnus	Regnault	Temperature	Magnus	Regnault
−20°	1.046	1.058	+1°	5.131	5.209
19	1.136	1.146	2	5.495	5.570
18	1.234	1.241	3	5.881	5.953
17	1.338	1.342	4	6.291	6.359
16	1.450	1.450	5	6.725	6.789
15	1.571	1.567	6	7.185	7.246
14	1.701	1.693	7	7.672	7.730
13	1.839	1.829	8	8.188	8.242
12	1.988	1.975	9	8.733	8.784
11	2.147	2.131	10	9.310	9.356
10	2.317	2.299	11	9.919	9.961
9	2.499	2.481	12	10.563	10.600
8	2.694	2.676	13	11.243	11.275
7	2.901	2.886	14	11.960	11.987
6	3.122	3.112	15	12.716	12.738
5	3.358	3.355	16	13.514	13.531
4	3.610	3.617	17	14.355	14.366
3	3.878	3.898	18	15.240	15.246
2	4.163	4.201	19	16.171	16.172
1	4.466	4.527	20	17.152	17.147
0	4.788	4.868			

Condensation of Vapour.—The results of experiments by Pasley on the condensation of aqueous vapour mixed with air on cold surfaces are summarised by O. Reynolds (*Proc. Roy. Soc.* xxi. 275) as follows: (1). The presence of a small quantity of air in aqueous vapour, produces considerable retardation in the condensation of the vapour on a cold surface. The condensability of pure vapour appears to depend only on the heat-conducting power of the condensing surface. (2). In conse-

quence of this action of the air, the size of the surface-condenser of a steam-engine must be increased according to the quantity of air mixed with the vapour. (3). By the mixture of air with steam before the latter comes to be used, the condensation may be diminished and the efficiency of the engine thereby impaired. (4). Nearly the greatest possible efficiency is attained, when the pressure of the air amounts to $\frac{1}{10}$ of that of the steam, or when about 2 cubic feet of air at 1 atm. at 15° are present to 1 pound of steam. According to Reynolds, the diminution of condensation of a vapour by admixture of air may be ascribed, as pointed out by Siemens, to the fact that the layer of air continually interposed between the condensing surface and the vapour must be penetrated or displaced by the latter before the condensation can go on.

HEAT OF CHEMICAL COMBINATION.

The principal data of Thermochemistry have been collected and arranged by Berthelot (*Annuaire pour l'An 1877, publié par le Bureau des Longitudes*, pp. 395-442) in the following tables. In the column headed 'Authors' M denotes Alluard; A, Andrews; B, Berthelot; D, Dulong; Ds, Desains; Dt, Ditté; Dev, Deville; F, Favre; G, Grassi; Gh, Graham; H, Hautefeuille; Hs, Hesse; L, Longuiné; P, Person; R, Regnault; T, Thomsen; Tr, Troost; S, Silbermann; W, Woods. Numbers not determined by experiment, but obtained according to analogy by calculation, are distinguished by a star. The numerical data denote kilogram-degrees, or thousands of gram-degrees.

TABLE I.—Formation of the most important Chemical Compounds, the Elements and Compounds being referred to the state in which they exist at 15°.

Compound	Constituents	Molecule	Heat evolved				Authors
			Gaseous	Liquid	Solid	In solution	
Hydrogen Chloride	H, Cl	36.5	+22.0	—	—	+39.3	T.
" Bromide	H, Br ⁽¹⁾	81	+8.1	—	—	+28.4	
" Iodide	H, I	128	+6.2	—	—	+13.2	
Water	H ² , O	18	+47.2	+69.0	+70.4	—	D, Hs., F. a. S.
Hydrogen Dioxide	H ² , O ²	34	—	—	—	+46.6	S. G., A., T., B.
" Sulphide	H ² , S	34	+4.6	—	—	+9.2	H., T.
" Selenide	H ² , Se	81	+5.4	—	—	—	H.
Ammonia	H ³ , N	17	+26.7	—	—	+35.2	J.
Hydroxylamine	H ³ , N, O	33	—	—	—	+47.4	B.
Acetylene (C≡Diam.)	C ² , H ²	26	+64.0	—	—	—	B.
Ethylene	C ² , H ⁴	28	+8.0	—	—	—	D., F. a. S., A., T.
Dimethyl or Ethane	2(C, H ³)	30	+28.0*	—	—	—	D., F. a. S., A.
Methane	C, H ⁴	16	+22.0	—	—	—	F. a. S. T.
Nitrogen Monoxide	N ² , O	44	+18.0	+13.6	—	—	B.
" Dioxide	N, O	30	+43.3	—	—	—	
" Trioxide	N ² , O ³	76	+65.6	—	—	+17.8	
" Tetroxide	N, O ²	46	+24.3	+20.0	—	—	
" Pentoxide	N ² , O ⁵	108	+44.6	+39.8	+31.6	+14.8	
Nitric Acid	{N, 2O, $\frac{1}{2}$ H ² O}	63	—	—	+14.6	+7.4	T.
Hyposulphurous Acid	S, O, H ² O	66	—	—	+19.9	+27.1	
Thiosulphuric Acid	S ² , O ² , H ² O	114	—	—	—	+17.4	
Sulphur Dioxide	S, O ²	64	+77.6	—	—	+85.2	D., Hs., F. a. S., A.
Sulphur Trioxide	S, O ³	80	—	—	+111.6	+149.4	D., Hs., F. a. S., A., T., B.
Sulphuric Acid	{SO ² , O, H ² O}	98	—	+54.4	—	+71.4	
	{S, O ² , H ² O}	98	—	+132.0	+133.0	+149.0	
	{S, O ⁴ , H ² }	98	—	+201.0	+202.0	+218.0	
Sulphuric Monohydrate	SO ⁴ H ² , H ² O	116	—	+6.2	+9.0*	—	B.
Phosphorus Pentoxide	P ² , O ⁵	142	—	—	+363.8	+405.4	T.
Arsenic Trioxide	As ² , O ³	198	—	—	+151.6	+147.0	
" Pentoxide	As ² , O ⁵	230	—	—	+219.4	+225.4	
Boron Trioxide (Amorphous B.)	B ² O ³	70	—	—	+317.2	+325.6	Tr. a. H.

(¹) The quantities of heat evolved, when both substances are assumed to be gaseous, are for HBr +12.4; for HI -0.6; for H²O +39.0; for H²S +7.2; for SO² +80.2; for CO² +69.0.

TABLE I.—*continued.*

Compound	Constituents	Molecule	Heat evolved				Authors
			Gaseous	Liquid	Solid	In solution	
Chlorine Monoxide	Cl_2, O	87	- 15.2	—	—	- 5.8	T. a. B.
" Trioxide	Cl_2, O_2	119	—	—	—	—	
" Tetroxide	Cl_2, O_4	135	—	—	—	—	
Chloric Acid	$\text{Cl}_2, \frac{1}{2}\text{O}_5 + \frac{1}{2}\text{H}_2\text{O}$	84.5	—	—	—	- 12.4	B.
Carbon Dioxide	C, O_2	44	+ 94.0	—	+ 100.0	+ 99.6	F. a. S.
C. Diamond			+ 97.0	—	+ 100.3	+ 102.6	
C. Amorphous	C, O	28	+ 25.0	—	—	—	F. a. S., G., A., J. B.
C. Diamond			+ 28.0	—	—	—	
Carbon Monoxide	C, S_2	76	- 15.6	- 9.2	—	—	F. a. S.
C. Diamond			- 12.6	- 6.2	—	—	
Carbon Disulphide	Si, O_2	60	—	—	+ 219.2	—	Tr. a. H.
C. Amorphous			—	—	+ 227.3	—	
Silica	Sn, O	134	—	—	+ 70.2	—	D., A., W.
Stannous Oxide	Sn, O_2	150	—	—	+ 141.2	—	D., A.
Stannic Oxide	N, Cl_3	120.5	—	- 38.1	—	—	D. a. H.
Nitrogen Chloride	P, Cl_3	137.5	+ 68.9	+ 75.8	—	—	B. a. L.
Phosphorus Trichloride	P, Br_3	271	—	+ 42.6	—	—	
" Tribromide	$\text{P}, \text{Cl}_3, \text{Cl}_2$	208.5	—	—	+ 07.8	—	A.
" Pentachloride			—	—	+ 32.0	—	
" Oxychloride	$\text{P}, \text{Cl}_3, \text{O}$	153.5	—	+ 142.1	—	—	T. a. H.
Arsenic Trichloride	$\text{P}, \text{Cl}_3, \text{O}$	153.5	—	+ 66.6	—	—	
Antimony Trichloride	As, Cl_3	181.5	+ 66.2	+ 74.6	—	—	D.
Boron Trichloride	B, Cl_3	117.5	+ 104.0	—	+ 86.3	—	
Silicon Trichloride	Si, Cl_4	170	—	+ 157.6	—	—	B.
Si. Amorphous			—	+ 165.7	—	—	
Si. Crystallised	C, N	26	+ 41.0	—	—	—	B.
Cyanogen (C. Diamond)	$\text{C}, \text{N}, \text{H}$	27	+ 14.1	- 8.1	—	+ 8.0	
Hydrogen Cyanide	$\text{C}, \text{N}, \text{K}$	65.1	—	—	+ 45.7	+ 42.9	B.
Potassium "	$\text{C}, \text{N}_2, \text{H}^+$	44	—	—	+ 32.7	+ 28.3	
Ammonium "	$2\text{C}, 2\text{N}, \text{H}_2$	252	—	—	- 20.4	- 23.4	B.
Mercury "	$\text{C}, \text{N}, \text{Ag}$	134	—	—	- 18.6	—	
Silver "	$\text{C}, \text{N}, \text{Cl}$	61.5	- 21.5	- 13.2	—	—	B.
Cyanogen Chloride	$\text{C}, \text{N}, \text{I}$	153	—	—	- 23.1	- 25.9	
" Iodide	$\text{C}, \text{N}, \text{K}, \text{O}$	81.1	—	—	+ 116.5	- 111.3	B.
Potassium Cyanate	O, O_2	—	- 29.6	—	—	—	
Ozone							

TABLE II.—*Formation of Solid Salts from Acid and Basic Oxides, both in the solid state.*

Nitrates			Sulphates		
$\text{N}_2\text{O}_5, \text{BaO}$.	+ 81.4	$\text{SO}_3, \text{H}_2\text{O}$.	+ 19.8
$\text{N}_2\text{O}_5, \text{SrO}$.	76.2	SO_3, BaO	.	102.0
$\text{N}_2\text{O}_5, \text{CaO}$.	59.2	SO_3, SrO	.	95.6
$\text{N}_2\text{O}_5, \text{PbO}$.	40.2	SO_3, CaO	.	84.0*
$\text{N}_2\text{O}_5, \text{Ag}_2\text{O}$.	38.4	SO_3, PbO	.	60.8
CO_2, BaO	.	50.0*	SO_3, ZnO	.	45.0
			SO_3, CuO	.	42.6
			$\text{SO}_3, \text{Ag}_2\text{O}$.	56.0

TABLE III.—*Formation of Solid Salts from Gaseous Acid Oxides and Solid Basic Oxides.*

N^2O^5 , BaO	+ 111.2	$(\text{C}^2\text{H}^2\text{O}^2)^2$, BaO	+ 70.0*
N^2O^5 , CaO	+ 67.6	CO^2 , BaO	+ 56.0

TABLE IV.—*Formation of Solid Salts from Solid Acids and Bases.*

Acid + Base = Salt + Water (solid).

Metals	Formate, HCO^2M	Acetate, $\text{CH}^3\text{CO}^2\text{M}$	Benzonate, $\text{C}^6\text{H}^5\text{CO}^2\text{M}$	Picrate, $\text{C}_{10}\text{H}^7(\text{NO}^2)_3\text{OM}$	Sulphate, $\frac{1}{2}\text{SO}^4\text{M}^2$	Oxalate, $\frac{1}{2}\text{C}_2\text{O}_4\text{M}^2$	Tartrate, $\frac{1}{2}(\text{CH}(\text{OH})\text{COO}^2\text{M})^2$
K	+ 25.5	+ 21.9	+ 22.5	+ 30.5	+ 81.4	+ 29.1	+ 27.1
Na	23.2	18.3	17.4	24.3	69.4	26.5	22.9
Ba	37.0	30.4	—	—	66.0	20.8 ⁽¹⁾	—
Sr	33.4	29.4	—	—	59.0	21.3 ⁽¹⁾	—
Ca	27.0	21.2	16.4	—	49.4	18.9 ⁽¹⁾	16.7 ⁽¹⁾
Mn	15.2	9.0	—	—	31.2	13.2 ⁽¹⁾	—
Zn	12.4	6.6	—	—	23.8	11.5 ⁽¹⁾	—
Cu	10.8	8.6	—	—	21.0	—	—
Pb	18.2	10.2	—	—	39.8	13.1	—
Ag	9.1	7.6	—	—	35.8	12.5	—

⁽¹⁾ These numbers relate to the precipitated hydrated salts.*Formation of Solid Ammonium Salts.*TABLE V.—*From Solid Acids and Gaseous Bases.*

Formic acid	HCO^2H	+ NH^3	+ 21.0
Acetic "	$\text{CH}^3\text{CO}^2\text{H}$	+ NH^3	18.5
Benzoic "	$\text{C}^6\text{H}^5\text{CO}^2\text{H}$	+ NH^3	17.0
Picric "	$\text{C}^6\text{H}^3(\text{NO}^2)_3\text{OH}$	+ NH^3	22.9
Sulphuric, "	$\frac{1}{2}\text{SO}^4\text{H}^2$	+ NH^3	33.8
Oxalic "	$\frac{1}{2}\{\text{CO}^2\text{H}\}$ $\frac{1}{2}\{\text{CO}^2\text{H}\}$	+ NH^3	24.4

TABLE VI.—*From Gaseous Acids and Gaseous Bases.*

Hydrochloric acid	HCl	+ NH^3	+ 42.5
Hydrobromic "	HBr	+ NH^3	45.6
Hydriodic "	HI	+ NH^3	44.2
Hydrocyanic "	$\text{H}(\text{CN})$	+ NH^3	20.5
Hydrosulphuric, "	H^2S	+ NH^3	23.0
Acetic "	$\text{C}^6\text{H}^5\text{CO}^2\text{H}$	+ NH^3	27.0*
Formic "	HCO^2H	+ NH^3	29.0
Nitric "	HNO^3	+ NH^3	30.0*

TABLE VII.—*From Acid Oxides, Water, and Bases, all three Gaseous.*

Nitrate	$\frac{1}{2}\text{N}^2\text{O}^5 + \frac{1}{2}\text{H}^2\text{O}$	+ NH^3	+ 47.1
Nitrite	$\frac{1}{2}\text{N}^2\text{O}^3 + \frac{1}{2}\text{H}^2\text{O}$	+ NH^3	33.7
Acetate	$\frac{1}{2}(\text{C}^2\text{H}^2\text{O}^2)^2\text{O} + \frac{1}{2}\text{H}^2\text{O}$	+ NH^3	41.0*
Acid Carbonate	$\text{CO}^2 + \text{H}^2\text{O}$	+ NH^3	30.4
Formate	$\text{CO}^2 + \text{H}^2\text{O}$	+ NH^3	31.6

TABLE VIII.—From the Gaseous Elements.

Ammonium Chloride . . .	Cl	+ H ¹ + N	+ 91.2
" Iodide . . .	I (gas.)	+ H ¹ + N	79.5
" Hydrosulphide . . .	S (gas.)	+ H ¹ + N	56.9
" Nitrite . . .	O ²	+ H ¹ + N ²	57.6
" Nitrate . . .	O ³	+ H ¹ + N ²	80.7
Hydroxylamine Hydrochloride .	Cl + H ¹	+ N + O	75.6

TABLE IX.—Formation of Metallic Oxides, according to Thomsen.

Constituents	Mol-ecule	Heat evolved		Constituents	Mol-ecule	Heat evolved	
		Solid	In solution			Solid	In solution
K, $\frac{1}{2}$ O, $\frac{1}{2}$ H ² O . . .	56.1	+ 69.8	+ 82.3	Fe, O . . .	72	+ 68.2	—
K, H, O . . .		104.3	116.8	Fe ² , O ³ . . .	160	191.2	—
Na, $\frac{1}{2}$ O, $\frac{1}{2}$ H ² O . . .	40	67.8	77.6	Zn, O . . .	81	85.4	—
Na, H, O . . .		102.3	112.1	Zn, O, H ² O . . .	99	82.6	—
Li, $\frac{1}{2}$ O, $\frac{1}{2}$ H ² O . . .	24	—	83.3	Cd, O . . .	128	65.6	—
Li, H, O . . .		—	117.8	Pb, O . . .	223	50.2	—
N, H ³ , H ² O . . .	35	—	35.2	Tl ² , O . . .	424	42.2	+ 39.2
N, H ³ , O . . .		—	104.2	Tl ² , O, H ² O . . .	442	45.4	39.2
Mg, O, H ² O . . .	58	149.0	—	Cu ² , O . . .	142.8	40.8	—
Mg, H ² , O ² . . .		218.0	—	Cu, O . . .	79.4	37.2	—
Al, $\frac{1}{3}$ O, $\frac{1}{3}$ H ² O . . .	78.4	194.4	—	Hg ² , O . . .	416	42.2	—
Mn, O . . .	71	94.8	—	Hg, O . . .	216	30.6	—
Mn, O ² . . .	87	116.2	—	Ag ² , O . . .	232	6.0	—
Mn ² , O ² , H ² O . . .	240	—	178.0				

TABLE X.—Formation of Metallic Chlorides, Bromides, and Iodides, according to Thomsen.

Constituents	Mol-ecule	Heat evolved		Constituents	Mol-ecule	Heat evolved	
		Solid	In solution			Solid	In solution
K, Cl . . .	74.6	+ 105.6	+ 101.2	K, Br . . .	119.1	+ 95.0	+ 89.4
Na, Cl . . .	58.5	97.7	96.8	K, I . . .	166.6	79.8	74.7
Li, Cl . . .	42.5	93.8	102.2	Pb, Br ² . . .	367	64.4	—
Mg, Cl ² . . .	95	151.0	187.0	Pb, I ² . . .	461	39.6	—
Al, Cl ³ . . .	132.9	160.9	237.8	Cu, Br . . .	143.4	25.0	—
Mn, Cl ² . . .	126	112.0	128.0	Cu, I . . .	190.4	16.3	—
Fe, Cl ² . . .	127	82.0	100.0	Cu, Br ² . . .	223.4	40.8	—
Fe, Cl ³ . . .	161.5	96.0	127.7	Hg, Br . . .	280	32.1	—
Zn, Cl ² . . .	136	97.2	112.8	Hg, I . . .	327	24.2	—
Cd, Cl ² . . .	183	93.2	96.2	Hg, Br ² . . .	360	50.6	—
Pb, Cl ² . . .	278	82.8	89.6	Hg, I ² . . .	454	34.4	—
Tl, Cl . . .	239.5	48.6	38.5	Ag, Br . . .	188	22.7	—
Cu, Cl . . .	98.9	32.9	—	Ag, I . . .	235	13.8	—
Cu, Cl ² . . .	134.4	51.6	62.6	KCN . . .	65.1	86.7	83.9
Hg, Cl . . .	235.5	41.3	—	Hg(CN) ² . . .	252	61.6	58.6
Hg, Cl ² . . .	271	63.2	59.8	Ag ₂ , Cu . . .	134	22.4	—
Ag, Cl . . .	143.5	29.4	—				

TABLE XI.—Formation of the most important Solid Salts of the Oxygen-acids from the Elements referred to their actual state, according to Berthelot.

Nitrates	{	N, O ³ , K	+ 97.0
		N, O ³ , Na	82.6
		N ² , O ³ , H ¹	80.7
		2N, 2O ³ , Pb	61.4
Sulphates	{	N, O ² , Ag	6.5
		S, O ⁴ , K ²	350.8
		S, O ⁴ , Na ²	335.0
		S, O ⁴ , Mg	309.0
		S, O ⁴ , Mn	256.2
		S, O ⁴ , Pb	222.6
		S, O ⁴ , Zn	242.0
		S, O ⁴ , Cu	191.4
Thiosulphate		S, O ⁴ , Ag ²	136.4
Carbonate		S ² , O ³ , K ²	274.8
(Carbon = Diamond).		C, O ³ , K ²	277.8
Formate		C, O ³ , Na ²	269.6
"		C, H, K, O ²	155.1
"		C, H, Na, O ²	150.6
Acetate		C ² , H ² , K, O ²	174.2
"		C ² , H ² , Na, O ²	168.6
Oxalate		C ² , K ² , O ¹	323.6
"		C ² , Na ² , O ¹	313.8

TABLE XII.—Heat of Formation of Organic Bodies from their Elements, Carbon crystallised, Hydrogen, Oxygen, and Nitrogen gaseous, calculated by Berthelot from the Heat of Combustion and other Data.

Cyanogen, gaseous	{	(CN) ²	- 82.0
Hydrocyanic Acid, gaseous	{	C ² , N ²	- 14.1
" liquid	{	C, N, H	- 8.4
Cyanogen Chloride, gaseous	{	C, N, Cl	- 21.5
" liquid	{	C, N, Cl	- 13.2
Cyanogen Iodide, solid		C, N, I	- 23.1
Potassium Formate		C, H, K, O ²	+ 155.1
" Acetate		C ² , H ² , K, O ²	+ 171.2
" Oxalate		C ² , K ² , O ²	+ 323.6
Formation of a higher Homologue		(A), C, H ²	+ 6.0
Conversion of Amorphous Carbon into } Diamond		C ²	+ 6.0
Carbon Monoxide (C = Diamond)		C, O	+ 25.0
Carbon Dioxide		C, O ²	+ 94.0
Acetylene		2(C ² H)	- 64.0
Ethylene		2(C ² H ²)	- 8.0
Dimethyl or Ethane		2(C ² H ³)	+ 14.0*
Methane		C, H ⁴	+ 22.0
Amylene, gaseous	{	C ³ , H ¹⁰	+ 5.4
" liquid	{	C ³ , H ¹⁰	+ 10.6
Diamylene		2(C ³ , H ¹⁰)	+ 11.8
Cetylene		C ¹⁶ , H ³²	+ 118.0
Lemon Oil		C ¹⁰ , H ¹⁶	+ 2.0
Turpentine Oil		C ¹⁰ , H ¹⁶	+ 17.0
Terbène		C ¹⁰ , H ¹⁶	+ 42.0
Benzene		C ⁶ , H ⁶	0*
Methyl Alcohol		C, H ⁴ , O	+ 62.0
Ethyl Alcohol		C ² , H ⁶ , O	+ 74.0
Propyl Alcohols, normal and pseudo-		C ³ , H ⁸ , O	+ 82.0*
Amyl Alcohol		C ⁵ , H ¹² , O	+ 96.0
Cetyl Alcohol, solid		C ¹⁸ , H ³⁶ , O	+ 112.0
Phenol		C ⁶ , H ⁶ , O	+ 34.0

TABLE XII.—continued.

Dextrose (grape-sugar)	C ⁶ , H ¹² , O ⁶	+ 265.0*
Ethyl Oxide	C ⁴ , H ¹⁰ , O	+ 53.0
Ethyl-amyl Oxide	C ⁷ , H ¹⁶ , O	+ 49.0*
Aldehyde, gaseous	C ² , H ⁴ , O	+ 46.0
" liquid	C ² , H ⁴ , O	+ 40.0
Acetone	C ³ , H ⁶ , O	+ 65.0
Normal Propyl Aldehyde	C ³ , H ⁸ , O	+ 69.0
Formic Acid, gaseous	C, H ² , O ²	+ 87.4
" liquid	C, H ² , O ²	+ 93.0
" solid	C, H ² , O ²	+ 95.5
Acetic Acid, gaseous	C ² , H ⁴ , O ²	+ 109.9
" liquid	C ² , H ⁴ , O ²	+ 116.0
" solid	C ² , H ⁴ , O ²	+ 118.4
Acetic Anhydride, liquid	C ⁴ , H ⁸ , O ³	+ 150.0
Butyric Acid, liquid	C ⁴ , H ⁸ , O ²	+ 155.0
Valeric Acid	C ⁵ , H ¹⁰ , O ²	+ 158.0
Palmitic Acid, liquid	C ¹⁶ , H ³² , O ²	+ 223.0
Oxalic Acid, solid	C ² , H ² , O ⁴	+ 197.0
Olein	C ³⁷ , H ⁷⁶ , O ⁶	+ 228.0*
Ethyl Chloride, gaseous	C ² , H ⁵ , Cl	+ 28.0*
" liquid	C ² , H ⁵ , Cl	+ 34.4*
Ethyl Iodide, gaseous (I, gaseous)	C ² , H ⁵ , I	+ 7.0*
" liquid (I, solid)	C ² , H ⁵ , I	+ 12.7*
Amyl Chloride, liquid	C ⁵ , H ¹¹ , Cl	+ 50.0
" Bromide	C ⁵ , H ¹¹ , Br	+ 34.0
" Iodide	C ⁵ , H ¹¹ , I	+ 19.5
Ethyl Nitrate	C ² , H ⁵ , N, O ³	+ 30.7
Acetyl Chloride	C ² , H ³ , Cl, O	+ 63.5
" Bromide	C ² , H ³ , Br, O	+ 53.6
" Iodide	C ² , H ³ , I, O	+ 39.0
Oxamide	C ² , H ⁴ , N ² , O ²	+ 169.0

TABLE XIII.—Formation of the principal Salts by means of very dilute acids (1 eq. acid dissolved in 2 or 4 litres of water at 15°), according to Berthelot and Thomsen.

Base	Hydrochloric acid HCl 1 eq. = 2 l.	Nitric acid HNO ³ 1 eq. = 2 l.	Acetic acid C ² H ³ O ² 1 eq. = 2 l.	Formic acid CHFO 1 eq. = 2 l.	Oxalic acid C ² H ² O ⁴ 1 eq. = 4 l.	Sulphuric acid SO ³ H ² 1 eq. = 4 l.	Hydrosulphuric acid H ² S 1 eq. = 16 l.	Hydrocyanic acid HCN 1 eq. = 2 l.	Carbonic Anhydride CO ² 1 eq. = 30 l.
Soda (1)	13.7	13.7	13.3	13.4	14.3	31.7	7.7	2.9	20.4
Potash	13.7	13.8	13.3	13.4	14.3	31.4	7.7	3.0	20.2
Ammonia	12.4	12.5	12.0	11.9	12.7	29.0	6.2	1.3	10.6
Lime (2)	28.0	27.8	26.8	27.0	37.0 (2)	31.2	7.8	—	19.6 (2)
Baryta (4)	27.7	27.8	26.8	27.0	33.4	36.8	—	—	22.2
Strontia (3)	28.0	27.8	26.6	27.0	35.2	30.8	—	—	21.0 (3)
Magnesia (3)	27.6 (2)	27.6 (2)	—	—	—	31.2	—	—	18.0
Manganous Oxide (2)	23.6	23.4	22.6 (2)	21.4	28.6	27.0	10.2 (2)	—	13.6 (2)
Ferrous Oxide	21.4	—	19.8	—	—	25.0	14.6	—	10.0
Zinc Oxide	19.6	19.6	17.8	13.2	25.0	23.4	19.2	—	10.0
Lead Oxide	15.4	15.4	13.0	13.2	25.6	21.4 (2)	26.6	—	13.4
	21.4	—	—	—	—	—	—	—	—
Cupric Oxide	15.0 (2)	15.0	12.4	—	—	18.4	31.6	—	4.8
Mercuric Oxide	18.9	—	—	—	—	—	48.7	31.0	—
Silver Oxide	—	5.2	4.7	—	12.9	14.4	55.8	20.9 (2)	13.8
	20.6 (2)	—	—	—	—	—	—	—	—
Alumina (2)	18.6	—	—	—	—	21.0	—	—	—
Ferric Oxide (2)	11.8	11.8	9.0	—	—	11.4	—	—	—

(1) 1 eq. = 2 l. (2) 1 eq. = 25 l. (3) Precipitated. (4) 1 eq. = 6 l. (5) 1 eq. = 10 (6) Crystallised.
 (7) 1 eq. = 4 l. (8) Very dilute. (9) Hydrate.

TABLE XIV.—*Formation of the Alkali-salts of Polybasic acids, according to Berthelot a. Thomsen (1 eq. of base dissolved in 2 litres of water, and every 1 vol. acid diluted with 1 vol. water at 15°).*

Acids	NaOH	KOH	NH ³	$\frac{1}{2}$ Ba(OH) ²
Sulphuric Acid, SO_3H^2	1NaOH 14.7 2NaOH 31.7	14.6 31.4	13.6 29.0	—
Oxalic Acid, $\text{C}^2\text{O}^4\text{H}^2$	1NaOH 13.8 2NaOH 28.6	13.8 28.6	— 25.4	—
Tartaric Acid, $\text{C}^4\text{O}^6\text{H}^2$	1NaOH 12.9 2NaOH 25.9	— —	— —	—
Carbonic Acid, (aqueous CO_2)	1NaOH 11.0 2NaOH 20.2	11.1 20.4	9.7 12.4 M or 10.6 (1)	—
Boric Anhydride, B^2O^3	1NaOH 11.6 2NaOH 19.8 (1) 1NaOH 12.6	— — —	8.9 11.6 11.2	—
Citric Acid, $\text{C}^3\text{H}^4\text{O}^3$	2NaOH 12.8 3NaOH 13.2 4NaOH 8 to 0 (1) 1NaOH 14.7	— — — —	11.2 11.5 0.2 13.5	13.4 14.3 0.7
Phosphoric Acid, PO^4H^3	2NaOH 11.6 3NaOH 7.3 4NaOH 1.6 (1)	— — —	12.8 or 9.3 (2) 6.8 or 0.2 (2) —	— — —
Periodic Acid, $\text{IO}^5\text{H}.2\text{H}^2\text{O}$	— — — —	1KOH 5.5 2KOH 12.4 3KOH 3.1 4KOH 3.1	— — — —	— — — —

(1) Variable according to concentration and excess of potash.

(2) 12.8 at first, afterwards 9.3, in consequence of spontaneous decomposition of dissolved salts; similarly 6.8 or 0.2 for 3 NH³.

TABLE XV.—*Formation of Ethers from Alcohols (the constituents being supposed to be in the state which they assume at ordinary temperatures) according to Berthelot.*

Alcohol + Acid = Ether + Water; Alcohol + Alcohol = Ether + Water.

Name	Formula	Heat evolved	
		Pure substance	Substance dissolved in water
Ethyl Chloride, liquid . . .	$\text{C}^2\text{H}^4\text{HCl}$	+ 3.4*	—
" Iodide	$\text{C}^2\text{H}^4\text{HI}$	+ 6.0*	—
" Acetate	$\text{C}^2\text{H}^3\text{C}^2\text{H}^3\text{O}^2$	— 2.0	— 1.8
" Oxalate	$(\text{C}^2\text{H}^3)^2\text{C}^2\text{O}^4$	— 3.8	— 3.5
" Succinic Acid (in solution).	$\text{C}^2\text{H}^4\text{C}^2\text{O}^4\text{H}^2$	—	— 3.6
Methyl Oxalate	$(\text{CH}^3)^2\text{C}^2\text{O}^4$	+ 1.6	— 2.4
Ethyl Nitrate	$\text{C}^2\text{H}^3\text{NO}^3$	+ 6.2	— 2.6
Nitroglycerin (insoluble) . . .	$\text{C}^3\text{H}^5(\text{NO}^3)^3$	+ 14.1	— 8.7
Nitromannite (insoluble) . . .	$\text{C}^3\text{H}^4(\text{NO}^3)^3$	+ 23.4	— 15.0
Ethyl Oxide	$\text{C}^2\text{H}^5(\text{C}^2\text{H}^5\text{O})$	— .3	+ 0.5
Methylsulphuric Acid	$\text{CH}^3(\text{SO}^4\text{H})$	+ 13.8 (1)	— 5.1
Ethylsulphuric Acid	$\text{C}^2\text{H}^3(\text{SO}^4\text{H})$	+ 14.7 (1)	— 4.7
Isethionic Acid	$\text{C}^2\text{H}^4\text{O}. \text{SO}^4$	+ 16.0 (1)	— 3.4
Propylsulphuric Acid	$\text{C}^3\text{H}^7.\text{SO}^4\text{H}$	+ 15.9 (1)	— 4.0
Isopropylsulphuric Acid	$\text{C}^3\text{H}^7.\text{SO}^4\text{H}$	+ 17.1 (1)	— 3.3
Isobutylsulphuric Acid	$\text{C}^4\text{H}^{10}.\text{SO}^4\text{H}$	+ 17.6 (1)	— 2.2
Amylsulphuric Acid	$\text{C}^5\text{H}^{11}.\text{SO}^4\text{H}$	+ 19.5 (1)	— 0.2
Glycerylsulphuric Acid	$\text{C}^3\text{H}^7\text{O}^2.\text{SO}^4\text{H}$	+ 15.2	— 3.2

(1) Alcohols and acids pure; alcoholic acids in dilute solution. (2) Refers both to the constituents and to the compounds.

TABLE XVI.—*Formation of Ethers and Alcohols in their Actual State from Hydrocarbons, according to Berthelot.*

	Constituents	Formula of Compound	Heat evolved	
			Hydro-carbon liquid	Hydro-carbon gaseous
Ethyl Alcohol	C^2H^6, H^2O gaseous	$C^2H^5(HO)$ { gaseous	—	16.9
	C^2H^6, H^2O liquid	liquid	—	26.5
Pseudopropyl Alcohol	C^3H^8, H^2O gaseous	$C^3H^7(HO)$ { liquid	—	16.9
	C^3H^8, H^2O liquid	solid	—	19.4
Conversion into Normal Propyl Alcohol	C^3H^8, H^2O liquid	$C^3H^7(HO)$ { liquid	—	26.1
	C^3H^8, H^2O (gaseous)	solid	—	16.5
Ethyl Oxide	C^2H^6, C^2H^6O (gaseous)	$C^2H^5(HO)$ { gaseous	—	0
	C^2H^6, C^2H^6O (liquid)	liquid	—	19.4
Amyl Chloride	C^5H^{12}, HCl	$C^5H^{11}(HCl)$ { dissolved	—	16.1
	C^5H^{12}, HBr	in water	—	22.0
Amyl Bromide	C^5H^{12}, HBr	$C^5H^{11}(HBr)$ { liquid	+ 17.6	22.9
	C^5H^{12}, HI	solid	+ 15.2	20.5
Ethylene Bromide	C^2H^4, Br^2 (liquid)	$C^2H^3Br^2$ { liquid	+ 14.8	20.0
	C^2H^4, Br^2 (gaseous)	solid	—	29.3
Ethyl Acetate	$C^2H^4, C^2H^3O^2$ (liquid)	$C^2H^3(C^2H^3O^2)$ { liquid	—	36.5
	$C^2H^4, C^2H^3O^2$ (gaseous)	solid	—	14.9
Ethylsulphuric Acid	C^2H^4, SO^2H^2 (pure)	$C^2H^3(SO^2H)$ { dilute	—	21.0
	C^2H^4, SO^2H^2 (dilute)	solid	—	31.5
Propylsulphuric Acid	C^3H^8, SO^2H^2 (pure)	$C^3H^7(SO^2H)$ { dilute	—	14.7
	C^3H^8, SO^2H^2 (dilute)	solid	—	33.6
Isethionic Acid	C^2H^4, SO^2H^2, H^2O	$C^2H^3(H^2O(SO^2H))$ { dilute	—	16.7
	C^2H^4, SO^2H^2 (dilute)	solid	—	53.3
Benzenesulphonic Acid	C^6H^6, SO^2H^2	$C^6H^5(H^2O(SO^2H))$ { dilute	+ 36.4 (°)	46.2 (°)
	C^6H^6, SO^2H^2 (dilute)	solid	+ 34.7	41.9
Toluenesulphonic Acid	C^7H^8, SO^2H^2	$C^7H^7(SO^2H)$ { dilute	— 2.6	3.6
	C^7H^8, SO^2H^2 (dilute)	solid	+ 35.9	—
Sodium Benzenesulphonate	$C^6H^6, SO^2H^2, NaOH$	$C^6H^5NaSO^2H + H^2O$ { solid	— 1.4	—
	$2C^6H^6, 2SO^2H^2, Ba(OH)^2$	$(C^6H^5)^2Ba(SO^2H)^2 + H^2O$ { solid	+ 60.3	—
Barium Benzenesulphonate	$2C^6H^6, 2SO^2H^2, Ba(OH)^2$	$(C^6H^5)^2Ba(SO^2H)^2 + H^2O$ { solid	+ 107.0	—
	$C^2H^4O, SO^2H^2, NaOH$	$C^2H^3(SO^2H)Na + H^2O$ { solid	+ 40.6 (°)	—
Sodium Ethylsulphate	$C^2H^4O, SO^2H^2, NaOH$	$(C^2H^3)^2(SO^2H)^2Ba + H^2O$ { solid	+ 66.4 (°)	—
Barium	$2C^2H^4O, 2SO^2H^2, Ba(OH)^2$			

(°) This compound is formed, not from the hydrocarbon, but from the alcohol.

TABLE XVII.—*Hydration of Oxides, Acid and Basic.*

Constituents	Compounds	Heat developed	Authors
$\frac{1}{2}N^2O^5$, solid, $\frac{1}{2}H^2O$ liquid	NO^2H	+ 1.2	B.
$\frac{1}{2}N^2O^5$ liquid, $\frac{1}{2}H^2O$ liquid	NO^2H	5.3	B.
SO^2 solid, H^2O liquid	SO^2H^2 { liquid	20.4	B.
	crystallised	21.2	B.
$\frac{1}{2}P^2O^5$, $\frac{1}{2}H^2O$	IO^2H crystallised	1.3	De.
$\frac{1}{2}P^2O^5$, $\frac{1}{2}H^2O$	PO^2H^2	16.9	T.
$\frac{1}{2}As^2O^5$, $\frac{1}{2}H^2O$	AsO^2H^2	3.4	T.
$\frac{1}{2}C^2H^4O^2$ liquid, $\frac{1}{2}H^2O$ liq.	$C^2H^3O^2$ { liquid	6.9	B. u. L.
	crystallised	9.4	B. u. L.
BaO , H^2O liquid	$Ba(OH)^2$	17.6	B.
SrO , H^2O	$Sr(OH)^2$	17.2	B.
CaO , H^2O	$Ca(OH)^2$	15.1	B.
PbO , H^2O	$Pb(OH)^2$	2.4	T.

TABLE XVIII.—*Formation of Aldehydes and Organic Acids by Oxidation, according to Berthelot.*

	Constituents	Compounds	Heat evolved	State of Aggregation
<i>From Hydrocarbons :</i>				
Ethyl Aldehyde . . .	C^2H^4, O	C^2H^4O	$\left\{ \begin{array}{l} + 48.0 \\ 54.6 \end{array} \right.$	$\left\{ \begin{array}{l} \text{gaseous} \\ \text{liquid} \end{array} \right.$
Normal Propyl Aldehyde .	C^3H^6, O	C^3H^6O	$\left\{ \begin{array}{l} 72.6 \\ 118.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{liquid} \\ \text{gaseous} \end{array} \right.$
Acetic Acid . . .	C^2H^4, O^2	$C^2H^4O^2$	$\left\{ \begin{array}{l} 124.0 \\ 121.5 \end{array} \right.$	$\left\{ \begin{array}{l} \text{liquid} \\ \text{solid} \end{array} \right.$
Oxalic Acid . . .	C^2H^2, O^4	$C^2H^2O^4$	$\left\{ \begin{array}{l} 261.0 \\ 111.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{solid} \\ \text{liquid} \end{array} \right.$
Acetic Acid . . .	C^2H^2, O, H^2O	$C^2H^4O^2$	$\left\{ \begin{array}{l} 113.5 \\ 140.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{solid} \\ \text{liquid} \end{array} \right.$
Formic Acid . . .	CH^4, O^3	$CH^2O^2.H^2O$	$\left\{ \begin{array}{l} 137.6 \end{array} \right.$	$\left\{ \begin{array}{l} \text{liquid} \\ \text{solid} \end{array} \right.$
<i>From Aldehydes :</i>				
Acetic Acid . . .	C^2H^4O, O	$C^2H^4O^2$	$\left\{ \begin{array}{l} 70.0 \\ 70.1 \end{array} \right.$	$\left\{ \begin{array}{l} \text{all the bodies} \\ \text{gaseous,} \end{array} \right.$
Propionic Acid . . .	C^3H^6O, O	C^3H^6O	$\left\{ \begin{array}{l} 74.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{actual stat.} \\ \text{,,} \end{array} \right.$
<i>From Alcohols :</i>				
Formic Acid, liquid . . .	CH^4O, O^2	$CH^2O^2.H^2O$	$\left\{ \begin{array}{l} 100.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$
Acetic Acid " . . .	C^2H^6O, O^2	$C^2H^4O^2.H^2O$	$\left\{ \begin{array}{l} 111.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$
Valeric Acid " . . .	$C^5H^{12}O, O^2$	$C^5H^{10}O^2.H^2O$	$\left\{ \begin{array}{l} 131.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$
Palmitic Acid, solid . . .	$C^{16}H^{34}O, O^2$	$C^{16}H^{32}O^2.H^2O$	$\left\{ \begin{array}{l} 180.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$
Oxalic Acid " . . .	C^2H^6O, O^3	$C^2H^2O^4.2H^2O$	$\left\{ \begin{array}{l} 261.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$
	$C^2H^4O^2, O^3$	$C^2H^2O^4.H^2O$	$\left\{ \begin{array}{l} 150.0 \end{array} \right.$	$\left\{ \begin{array}{l} \text{,,} \end{array} \right.$

TABLE XIX.—*Various Organic Compounds according to Berthelot.*

Names			Heat evolved
<i>Formation of Amides, from Ammonium salts :</i>			
Formamide . . .	$CH^4O^2NH^4$ aq.	CH^4NO aq.	-- 1.0
Formonitril . . .	$CH^4O^2NH^4$ aq.	CHN aq.	-- 10.4
Hydrocyanic Acid . . .	$C^2H^2O^4(NH^2)^2$ cryst.	$C^2H^4N^2O^2$ solid	-- 2.4
Oxamide . . .			
<i>Formation of Polymeric Compounds :</i>			
Diamylene . . .	$2C^5H^{10}$ $\left\{ \begin{array}{l} \text{liquid} \\ \text{gaseous} \end{array} \right.$	$C^{10}H^{20}$ $\left\{ \begin{array}{l} \text{liquid} \\ \text{gaseous} \end{array} \right.$	$\left\{ \begin{array}{l} + 11.8 \\ + 22.3 \end{array} \right.$
Benzene . . .	$3C^6H^2$	$C^{18}H^6$ gaseous	+ 190.0*
<i>Formation of the Chlorides of Acid Radicles (E. a. L.):</i>			
Pure Acid + HCl gaseous = Acid Chloride liquid + H ² O liquid.			
Acetyl Chloride . . .	—	C^2H^2OCl	-- 5.5
" Bromide . . .	—	C^2H^2OBr	-- 2.0
" Iodide . . .	—	C^2H^2OI	-- 1.8
Butyryl Chloride . . .	—	C^4H^7OCl	-- 3.8
" Bromide . . .	—	C^4H^7OBr	-- 1.9
Valeryl Chloride . . .	—	C^5H^9OCl	-- 2.5
" Bromide . . .	—	C^5H^9OBr	-- 1.7

The following are thermochemical determinations, chiefly by Berthelot and Thomsen, not included in the preceding table; and re-determinations of certain values contained therein. The heat-unit is the kilogram-degree, excepting where the contrary is stated.

Thermic Constants of Oxidising and Reducing Agents (Thomsen, *Deut. Chem. Ges. Ber.* vi. 233, 1431). The thermochemical determination of the strength of affinity of oxygen in the several stages of oxidation of a body requires an exact knowledge of the action of oxidising and reducing agents: for only a small number of oxygen-compounds can be directly prepared in such a manner that the oxidation can be made the basis of exact calorimetric determinations. In most cases, indeed, the heat has to be estimated by indirect methods, either by oxidation with the aid of oxidising agents, or by subjecting the oxidised compound under examination to the action of reducing agents. With this view, Thomsen has determined the following constants:—

Reaction-constants of Reducing Agents.

Reaction	Q (heat evolved)
(SO ² Aq, Cl ²)	73·907
(Fe ² Cl ² II ¹ Aq, Cl ²)	55·523
(2FeSO ⁴ Aq, Cl ²)	48·763
(SnCl ⁴ H ¹ Aq, Cl ²)	76·019
(SO ² Aq, O)	63·634
(Fe ² Cl ² II ¹ Aq, O)	45·250
(2FeSO ⁴ Aq, O)	38·490
(SnCl ⁴ H ¹ Aq, O)	65·746

The meaning of these numbers is as follows: If one of these reducing agents, sulphurous acid, ferrous sulphate, ferrous chloride, stannous chloride, be used to remove oxygen or chlorine from a compound, and if the quantity of heat evolved in this process for every atom of oxygen or molecule of chlorine removed be denoted by R, then the quantity of heat consumed in the decomposition of the compound which furnishes the oxygen or chlorine, is represented by Q - R.

Reaction-constants of Oxidising Agents.

Reaction	Q = total heat evolved	Number of oxygen atoms given off	Q for 1 oxygen atom
2(Cl, H, Aq) - (H ² , O)	10·273 heat-units	1	10·273 gram-degrees
2(Br, H, Aq) - (H ² , O)	-11·605	1	-11·605
2(Br, Aq, H) - (H ² , O)	-12·683	1	-12·618
(Cl, H, Aq) - (Cl, O, H, Aq)	9·437	1	9·437
(Mn ² O ³ K ² Aq, 6HClAq)	58·635	5	11·727
(Mn ² O ³ K ² Aq, 3SO ³ Aq)	69·485	5	13·897
(Mn ² O ³ K ² Aq, 2HClAq)	55·757	3	18·556
(Mn ² O ³ K ² Aq, SO ³ Aq)	59·547	3	19·849
(MnO, SO ³ Aq) *	4·969	1	4·969
(2CrO ³ Aq, 3SO ³ Aq)	30·452	3	10·151
-(2MnO, O ² , 2KAq)	28·257	3	9·419
-(2MnO ² , 2KAq)	-14·765	5	-2·953
-(Mn, O)	-21·511	1	-21·511
-(2Cr, O ² , Aq)	-18·868	3	-6·299
-(IIAq, O ²)	-42·542	3	-14·181
-(H ² O, O, Aq)	+23·074	1	+23·074

The meaning of these numbers is as follows: If a substance is oxidised by one of the reagents here indicated, viz. chlorine, bromine, potassium permanganate, manganese

* K = KHO; Mn = MnH²O³; Cr = CrH²O³.

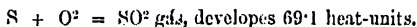
dioxide, chromic acid, or hydrogen dioxide, the quantity of heat developed by each atom of oxygen absorbed is greater by the value of Q given in the table for the reagent in question, than that which would have been developed if the same oxidation had been effected by oxygen. If the oxidation effected by either of these reagents be equal to R heat-units for 1 atom of oxygen, then the quantity which would be evolved by oxidation with free oxygen is $R - Q$.

Heat of Combustion of Hydrogen. Schüller a. Wartha (*Ber.* xi. 1298), by means of their modified form of Bunsen's ice-calorimeter (p. 926), estimate the quantity of heat evolved by the combustion of 1 gram of hydrogen (at 0° and 760 mm.) at 34.126 heat-units. (Thomson's number 69 [p. 952] denotes the quantity evolved in the combustion of 2 grams of hydrogen.)

C. v. Than (*Ber.* xi. 947, 1241) has determined the quantity of heat evolved in the combustion of a mixture of 2 vol. H. and 1 vol. O. in closed vessels, by burning a measured quantity of the gas in Bunsen's ice-calorimeter. The number thus found in one experiment was 33.863 heat-units; another, in which additional precautions were taken to ensure the correct measurement of the gas, gave 33.964 units.

Heat of Formation of Ozone. According to Berthelot (*Compt. rend.* lxxxii. 1281), the formation of ozone from oxygen under the influence of the silent electric discharge is attended with an absorption of heat amounting to 29.6 units.

Heat of Combustion of Sulphur. According to Berthelot (*Compt. rend.* lxxxiv. 674):



On account however of the unavoidable formation of SO^3 , the true number must be a little lower than this. The experiment was made with pure octohedral sulphur. The insoluble sulphur extracted from flowers of sulphur would yield the same amount of heat, since its conversion into octohedral sulphur, which takes place at about 18° , is not attended either with evolution or with absorption of heat.

Sulphuric Acid and Sulphates. Berthelot (*loc. cit.*) deduces the heat of formation of these compounds from the following data, which he regards as the most exact yet obtained:

	Heat-units
$S + O^2 = SO^2 \text{ gas}$	69.1 (Berthelot)
$SO^2 \text{ gas} + \text{water} = SO^2 \text{ dissolved}$	7.7 (Favre, Thomson)
$SO^2 \text{ dissolved} + Cl^2 \text{ gas} + 2H^2O = SO^3.H^2O \text{ dilute}$	73.9 (Thomson)
$H + Cl = HCl \text{ dilute}$	39.3 (Thomson)
$H^2 + O = H^2O$	69.0 (mean acc. to several observers)

Hence:

	Heat-units
$SO^2 \text{ dissolved} + O + H^2O + \text{water} = SO^3.H^2O \text{ dilute}$	64.3
$SO^2 \text{ gas} + O + H^2O + \text{water} = SO^3.H^2O \text{ dilute}$	72.0
$S + O^3 + H^2O = SO^3.H^2O \text{ dilute}$	141.0

Further.

$SO^3 + \text{water} = SO^3.H^2O \text{ dilute}$	37.4 (Berthelot)
$SO^3.H^2O \text{ pure} + \text{water} = SO^3.H^2O \text{ dilute}$	17.0 (various)

whence:

$S + O^3 = SO^3 \text{ anhydrous}$	103.6
$SO^2 + O = SO^3$	34.4
$S + O^3 + H^2O = SO^3.H^2O$	124.0
$S + O^1 + H^2 = SO^3.H^2$	193.0

Finally, according to various investigators:

$S + O^1 + K^2 = SO^1K^2$	342.2
$S + O^1 + Na^2 = SO^1Na^2$	326.4
$S + O^1 + Pb = SO^1Pb$	214.0
$S + O^1 + Zn = SO^1Zn$	233.4
$S + O^1 + Cu = SO^1Cu$	182.8

For the heat of formation of potassium thiosulphate, Berthelot finds (*Compt. rend.* lxxxii. 400):



Hyposulphurous acid, SO^2H^2 (Berthelot, *ibid.* lxxxiii. 416):

	Heat-units
$\text{S} + \text{H}^2 + \text{O}^2 + \text{water} = \text{SO}^2\text{H}^2 \text{ dilute}$	+ 86.4
$\text{S} + \text{H}^2\text{O}^2 = \text{SO}^2\text{H}^2$	39.0
$\text{SO}^2 + \text{H}^2 + \text{water} = \text{SO}^2\text{H}^2$	0.6
$\text{H}^2\text{S} \text{ dil.} + \text{O}^2 = \text{SO}^2\text{H}^2$	38.6
$2\text{SO}^2\text{H}^2 \text{ dil.} = \text{SO}^4\text{H}^2 \text{ dil.} + \text{SH}^2 \text{ dissolved}$	54.8
$2\text{SO}^2\text{H}^2 = \text{S}^2\text{O}^2\text{H}^2$	41.2

This last value explains the greater stability of thiosulphuric acid, $\text{S}^2\text{O}^2\text{H}^2$, inasmuch as the stability of a chemical system increases, under otherwise similar circumstances, with the amount of energy which it has lost.

Heat of Formation of Hydrobromic and Hydriodic Acids (Berthelot, *Compt. rend.* lxxxv. 677, 678).

For Hydrobromic acid, Berthelot finds—

$\text{H} + \text{Br liquid} = \text{HBr gas}$	9.5
$\text{H} + \text{Br solid} = \text{HBr}$	9.4
$\text{H} + \text{Br gas} = \text{HBr}$	13.5
$\text{H} + \text{Br liquid} + \text{water} = \text{HBr dissolved}$	29.5
$\text{H} + \text{Br gas} + \text{water} = \text{HBr dilute}$	33.1

For Hydriodic acid:

$\text{H} + \text{I solid} = \text{HI gas}$	- 6.4
$\text{H} + \text{I liquid} = \text{HI}$	- 4.5
$\text{H} + \text{I gas} = \text{HI}$	- 0.8
$\text{H} + \text{I solid} + \text{water} = \text{HI dilute}$	+ 13.2
$\text{H} + \text{I gas} + \text{water} = \text{HI}$	+ 18.8

The numbers for the heats of formation of hydrochloric acid (22.0, p. 252) and of hydrobromic acid are nearly on the ratio of 1 : 2.

Thermochemistry of the Oxygen-acids of Chlorine, Bromine, and Iodine. 1. *Chloric acid and Chlorates* (Berthelot, *Ann. Chim. Phys.* [5], x 327-389).

1. Formation of Chlorates from the Elements:

$\text{Cl} + \text{O}^3 + \text{K} = \text{ClO}^3\text{K solid}$	94.6
$\text{Cl} + \text{O}^3 + \text{Na} = \text{ClO}^3\text{Na}$	85.4

Various Reactions:

$3\text{Cl}^2 + 3\text{K}^2\text{O dilute} = 3\text{ClO}^3\text{K dilute} + 3\text{KCl dilute}$	+ 76.2
$3\text{Cl}^2 + 3\text{Na}^2\text{O} = 3\text{ClO}^3\text{Na} + 3\text{NaCl}$	+ 75.9
$3\text{Cl}^2 + \frac{3}{2}\text{BaO} = 3\text{ClO}^3\text{Ba}^{\frac{1}{2}} + \frac{3}{2}\text{BaCl}^2$	+ 75.1
$3\text{Cl}^2 + 3\text{K}^2\text{O} = \text{ClO}^3\text{K diss.} + 5\text{KCl}$	+ 94.2
$3\text{Cl}^2 + 3\text{Na}^2\text{O} = \text{ClO}^3\text{Na} + 5\text{NaCl}$	+ 94.2
$3\text{Cl}^2 + 3\text{BaO} = \text{ClO}^3\text{Ba}^{\frac{1}{2}} + \frac{5}{2}\text{BaCl}^2$	+ 95.0
$3\text{Cl}^2 + 3\text{K}^2\text{O} = 6\text{KCl} + \text{O}^3$	+ 111.0
$3\text{Cl}^2 + 3\text{Na}^2\text{O} = 6\text{NaCl} + \text{O}^3$	+ 110.0
$3\text{Cl}^2 + 3\text{BaO} = 3\text{BaCl}^2 + \text{O}^3$	+ 111.8
$3\text{ClO}^3\text{K dissolved} = \text{ClO}^3\text{K} + 2\text{KCl}$	+ 18.0
$3\text{ClO}^3\text{Na} = \text{ClO}^3\text{Na} + 2\text{NaCl}$	+ 18.3
$3\text{ClO}^3\text{Ba}^{\frac{1}{2}} = \text{ClO}^3\text{Ba}^{\frac{1}{2}} + \text{BaCl}^2$	+ 19.9

Successive oxidation:

$\text{Cl}^2 + \text{O} + \text{water} = \text{Cl}^2\text{O dilute}$	- 5.8
$\text{Cl}^2 + \text{O}^3 + \text{water} = \text{Cl}^2\text{O}^3$	- 24.0

Heat of conversion of chlorates into chlorides and oxygen:

$\text{KClO}^3 \text{ solid} = \text{KCl solid} + \text{O}^3$	+ 11
$\text{NaClO}^3 = \text{NaCl} + \text{O}^3$	+ 12.3
$\text{Ba}^{\frac{1}{2}}\text{ClO}^3 = \text{Ba}^{\frac{1}{2}}\text{Cl} + \text{O}^3$	12.6

Heat of solution of potassium perchlorate:

$\text{ClO}^4\text{K} + 100 \text{ times its weight of water at } 23^\circ$	- 12.13
-----------------------------------------------------------------------------	---------

2. Bromic acid (*Compt. rend.* lxxxiv. 679).

	Heat-units
$\text{Br}^{\text{liq}} + \text{O}^{\text{s}} + \text{H}^{\text{2O}} + \text{water} = \text{Br}^{\text{O}^{\text{s}}}\text{H}^{\text{2O}} \text{ dilute}$	- 49.6
$\text{Br}^{\text{gas}} + \text{O}^{\text{s}} + \text{H}^{\text{2O}} + \text{water} = \text{Br}^{\text{O}^{\text{s}}}\text{H}^{\text{2O}}$	- 42.2
$\text{Br}^{\text{O}^{\text{s}}}\text{H} \text{ dilute} = \text{HBr} \text{ dilute} + \text{O}^{\text{s}}$	+ 15.5
$\text{Br}^{\text{O}^{\text{s}}}\text{K} \text{ solid} = \text{KBr} \text{ solid} + \text{O}^{\text{s}}$	+ 11.1

Formation of hypobromites with excess of alkali:

$\text{Na}^{\text{2O}} (1 \text{ eq. in 3 litres}) + \text{Br}^{\text{2}} \text{ at } 9^{\circ}$	+ 12.0
$\text{K}^{\text{2O}} (\quad \quad \quad) + \text{Br}^{\text{2}} \text{ at } 11^{\circ}$	+ 11.9
$\text{BaO} (\quad \quad \quad) + \text{Br}^{\text{2}} \text{ at } 13^{\circ}$	+ 11.4

Supposing now that dilute hypobromous acid in combining with bases gives out as much heat as hypochlorous acid, namely, 9.5 units; then, for the heat of formation of hypobromous acid, we have:

$\text{Br}^{\text{2}} \text{ liquid} + \text{O} + \text{water} = \text{Br}^{\text{O}} \text{ dilute}$	- 13.4
$\text{Br}^{\text{2}} \text{ gas} + \text{O} + \text{water} = \text{Br}^{\text{O}}$	- 6.0

3. Iodic acid and Iodates (*Berthelot, Compt. rend.* lxxxiv. 734).

$\text{I}^{\text{2}} \text{ solid} + \text{O}^{\text{s}} + \text{water}$	$= \text{IO}^{\text{3}}\text{H} \text{ dilute}$	+ 45.2
$\text{I}^{\text{2}} \text{ " } + \text{O}^{\text{s}}$	$= \text{I}^{\text{2}}\text{O}^{\text{5}} \text{ anhydrous}$	+ 46.8
$\text{I}^{\text{2}} \text{ gas} + \text{O}^{\text{s}}$	$= \text{I}^{\text{2}}\text{O}^{\text{5}} \text{ solid}$	+ 37.8
$\text{I}^{\text{2}} \text{ solid} + \text{O}^{\text{6}} + \text{H}^{\text{2}} + \text{water}$	$= 2\text{IO}^{\text{3}}\text{H} \text{ dissolved}$	+ 114.2
$\text{I}^{\text{2}} \text{ " } + \text{O}^{\text{6}} + \text{H}^{\text{2}}$	$= 2\text{IO}^{\text{3}}\text{H} \text{ crystallised}$	+ 119.6
$\text{I}^{\text{2}}\text{O}^{\text{5}} \text{ solid} + \text{H}^{\text{2}}\text{O} \text{ solid}$	$= 2\text{IO}^{\text{3}}\text{H}$	+ 2.26
$\text{I}^{\text{2}}\text{O}^{\text{5}} \text{ " } + 2\text{IO}^{\text{3}}\text{H}$	$= 2\text{IO}^{\text{3}}\text{H} \cdot \text{I}^{\text{2}}\text{O}^{\text{5}}$	+ 1.24
$\text{IO}^{\text{3}}\text{H} \text{ dissolved}$	$= \text{HI} + \text{O}^{\text{s}}$	- 43.9
$\text{IO}^{\text{3}}\text{H} \text{ cryst.} + \text{KOH} \text{ solid}$	$= \text{IO}^{\text{3}}\text{K} \text{ cryst.} + \text{H}^{\text{2O}} \text{ solid}$	+ 31.5
$\text{IO}^{\text{3}}\text{K} \text{ " } + \text{IO}^{\text{3}}\text{H}$	$= \text{IO}^{\text{3}}\text{K} \cdot \text{IO}^{\text{3}}\text{H} \text{ solid}$	+ 3.1
$\text{I} \text{ solid} + \text{O}^{\text{s}} + \text{K}$	$= \text{IO}^{\text{3}}\text{K} \text{ solid}$	+ 123.9
$\text{I} \text{ gas} + \text{O}^{\text{s}} + \text{K}$	$= \text{IO}^{\text{3}}\text{K}$	+ 128.4
$\text{IO}^{\text{3}}\text{K} \text{ solid}$	$= \text{KI} \text{ " } + \text{O}^{\text{s}}$	- 44.1
$\text{IO}^{\text{3}}\text{K} \text{ dissolved}$	$= \text{KI} \text{ dissolved} + \text{O}^{\text{s}}$	- 43.4

The heat of formation of potassium iodate is greater than that of the bromate or chlorate.

$\text{I} \text{ gas} + \text{O}^{\text{s}} + \text{K}$	$= \text{IO}^{\text{3}}\text{K} \text{ solid}$	+ 128.4
$\text{Cl} \text{ gas} + \text{O}^{\text{s}} + \text{K}$	$= \text{ClO}^{\text{3}}\text{K}$	+ 94.6
$\text{Br} \text{ gas} + \text{O}^{\text{s}} + \text{K}$	$= \text{BrO}^{\text{3}}\text{K}$	+ 87.6

Hence it appears that the stability of the three salts increases from the bromate to the chlorate and iodate. The greater stability of the iodate is indicated also by a comparison of the heats of decomposition of the three salts:

$\text{ClO}^{\text{3}}\text{K} = \text{KCl} + \text{O}^{\text{s}}$	+ 11
$\text{BrO}^{\text{3}}\text{K} = \text{KBr} + \text{O}^{\text{s}}$	+ 11.1
$\text{IO}^{\text{3}}\text{K} = \text{KI} + \text{O}^{\text{s}}$	- 44.1

A comparison of the fundamental reactions of the three halogens with an alkali gives:

$3\text{Cl}^{\text{2}} \text{ gas} + 3\text{K}^{\text{2O}}$	$\left\{ \begin{array}{l} 3\text{ClOK} \text{ diss.} + 3\text{KCl} \text{ dissolved} \\ \text{ClO}^{\text{3}}\text{K} \\ 6\text{KCl} \text{ " } + \text{O}^{\text{s}} \end{array} \right.$	$\left\{ \begin{array}{l} + 76.2 \\ + 94.2 \\ + 111.0 \end{array} \right.$
$3\text{Br}^{\text{2}} \text{ gas} + 3\text{K}^{\text{2O}}$	$\left\{ \begin{array}{l} 3\text{BrOK} \text{ " } + 3\text{KBr} \text{ " } \\ \text{BrO}^{\text{3}}\text{K} \text{ " } + 5\text{KBr} \text{ " } \\ 6\text{KBr} \text{ " } + \text{O}^{\text{s}} \end{array} \right.$	$\left\{ \begin{array}{l} + 57.6 \\ + 54.0 \\ + 74.4 \end{array} \right.$
$3\text{I}^{\text{2}} \text{ gas} + 3\text{K}^{\text{2O}}$	$\left\{ \begin{array}{l} 3\text{IOK} \text{ " } + 3\text{KI} \text{ " } \\ \text{IO}^{\text{3}}\text{K} \text{ " } + 5\text{KI} \text{ " } \\ 6\text{KI} \text{ " } + \text{O}^{\text{s}} \end{array} \right.$	$\left\{ \begin{array}{l} + 19.5 \\ + 26.4 \\ - 17.6 \end{array} \right.$

From this it is seen that the most important chemical conditions in the formation of compounds of oxygen with the halogen-elements are in accordance with the thermic relations.

Heat of Formation and Transformation of Hydroxylamine, or Ox-ammonia, NH^2O (Berthelot, *Compt. rend.* lxxiii. 473):

NH^2O dissolved	$= \frac{2}{3}\text{N} + \frac{1}{3}\text{NH}^2\text{O}$ dissolved	+ Heatunits	+ 57.0
NH^2O	+ HCl dilute at 24°		+ 9.2
$\text{NH}^2\text{O.HCl}$	cryst. + 90 pts. water at 24°		- 2.31
$\text{N} + \text{H}^2 + \text{O}$	$= \text{NH}^2\text{O}$ dissolved		+ 23.7*
$\text{N} + \text{H}^2 + \text{O} + \text{HCl}$ dil.	$= \text{NH}^2\text{O.HCl}$ dissolved		+ 39.5
$\text{N} + \text{H}^2 + \text{O}$ (l)	$= \text{NH}^2\text{O.HCl}$ cryst.		+ 75.5
$\text{NO} + \text{H}^2$	$= \text{NH}^2\text{O}$ dissolved		+ 67.0

For the purely theoretical reactions:

NH^2O dissolved	+ $\text{O} = \text{NH}^2\text{O}$ dissolved	- 11.2
$\text{NH}^2\text{O.HCl}$ solid	+ $\text{O} = \text{NH}^2\text{O.HCl}$ cryst.	- 15.1

Further:

NH^2O diss.	+ $\text{H}^2 = \text{NH}^2\text{O}$ diss.	+ 67.0
NH^2O dil.	+ $\frac{1}{2}\text{O} = \text{N} + \frac{3}{2}\text{H}^2\text{O}$	+ 79.8
NH^2O	+ $\text{O} = \text{NO}^2 + \frac{3}{2}\text{H}^2\text{O}$ liquid	+ 70.8
NH^2O	+ $\text{O}^2 = \text{NO}^2$ dil. + $\frac{3}{2}\text{H}^2\text{O}$	+ 53.9
NH^2O	+ $\text{O}^2 = \text{NO}^2$ " + $\frac{3}{2}\text{H}^2\text{O}$	+ 72.4
$\text{NH}^2\text{O.HCl}$ diss.	+ $\frac{1}{2}\text{K}^2\text{O}$ " " " "	+ 4.44
"	+ NH^2 " " " "	+ 3.2

Decomposition of Ammonium Nitrate (Berthelot, *Ann. Chim. Phys.* [5], x. 364).

$\text{NO}^2\text{H.NH}^2$ solid	$= \text{N}^2\text{O} + 2\text{H}^2\text{O}$ liquid	37.3
"	fused $= \text{N}^2\text{O} + 2\text{H}^2\text{O}$ gas, about	26.0
"	" $= \text{N}^2 + \text{O} + 2\text{H}^2\text{O}$ gas	44.0
"	" $= \text{N} + \text{NO} + 2\text{H}^2\text{O}$ gas	1.0
"	" $= \frac{2}{3}\text{N} + \frac{1}{3}\text{NO}^2 + 2\text{H}^2\text{O}$ gas	32.0
"	" $= \text{NO}^2\text{H}$ gas + NH^2 gas	-30.0

Heat of Formation of various Metallic Compounds.* 1. Magnesium, Calcium, Strontium and Barium (Thomson, *J. pr. Chem.* [2], xvi. 97-124).

Reaction	Magnesium	Calcium	Strontium	Barium
(R, O)	145.86	131.36	130.98	130.38
(R, O, H^2O)	148.96	146.46	148.18	148
(R, O, Aq.)	—	149.46	157.78	158.26
(R, O^2 , W^2O^2)	—	207.21	223.83	229.72
(R, O^2 , SO^2)	232.31	248.97	259.82	266.49
(R, Cl^2)	151.01	170.23	184.55	194.25
(R, Br^2)	—	141.25	157.7	169.46
(R, I^2)	—	107.65	—	—
(R, Cl^2 , $6\text{H}^2\text{O}$)	183.98	191.98	203.19	—
(R, Br^2 , $6\text{H}^2\text{O}$)	—	166.85	181.01	—
(R, Cl^2 , $2\text{H}^2\text{O}$)	—	—	—	201.25
(R, Br^2 , $2\text{H}^2\text{O}$)	—	—	—	178.57
(R Cl^2 , Aq.)	35.92	17.41	11.14	2.07
(R Br^2 , Aq.)	—	24.61	16.11	4.98
(R I^2 , Aq.)	—	27.69	—	—
(R, Cl^2 , Aq.)	186.93	187.64	195.69	196.32
(R, Br^2 , Aq.)	165.05	165.76	173.81	174.44
(R, I^2 , Aq.)	134.63	135.84	143.39	144.02
(R Cl^2 , $6\text{H}^2\text{O}$)	32.97	21.75	18.64	—
(R Br^2 , $6\text{H}^2\text{O}$)	—	25.60	23.31	—
(R Cl^2 , $2\text{H}^2\text{O}$)	—	—	—	7
(R Br^2 , $2\text{H}^2\text{O}$)	—	—	—	9.11
(R O^2H^2 Aq., 2HCl Aq.)	27.69	27.90	27.63	27.78
(R O^2H^2 Aq., SO^2 Aq.)	31.22	31.14	30.71	36.9

On the Heat of Solution of these salts, see pp. 991, 992.

* In the table (p. 952) the thermal value given for this reaction is 47.4.

2. Nickel and Cobalt compounds (Thomsen, *J. pr. Chem.* [2], xiv. 413). These metals in their dynamic relations stand nearest to iron, the order of affinity being Fe—Co—Ni. The heat of formation of the monoxides, sesquioxides and anhydrous chlorides is shown in the following table:—

R	(R, O, H ² O)	(R ² , O ³ , 3H ² O)	(RCl ³)
Fe . . .	68.28 heat-units	191.13 units	82.05 units
Co . . .	63.47 "	149.30 "	76.48 "
Ni . . .	60.84 "	120.38 "	74.53 "

The analogy of the three metals is shown by their heat of neutralisation, and the evolution of heat on solution of the anhydrous chlorides in water—

R	(RO ² H ² , SO ³ Aq.)	(RO ² H ² , 2HClAq.)	(RCl ³ , Aq.)
Fe . . .	24.92 units	21.39 units	17.90 units
Co . . .	24.67 "	21.14 "	18.34 "
Ni . . .	26.11 "	22.58 "	19.17 "

The difference between the three is shown by the evolution of heat on formation of the sesquioxides from the monoxides:—

R	(2RO ² H ² , O, H ² O)
Fe . . .	54.57 heat-units
Co . . .	22.5 "
Ni . . .	1.3 "

It is owing to this difference that iron sesquioxide dissolves in dilute sulphuric acid without decomposition, whilst cobalt sesquioxide gives off oxygen, with formation of a cobaltous salt, and in the case of nickel the decomposition is very energetic. For the same reason the acid solutions of nickel and cobalt sulphates are not oxidised in the air. On the other hand, the free monoxides or their ammoniacal solutions behave quite differently—the oxidation of iron monoxide being represented by 54570 heat-units, that of cobalt monoxide by 22500 units, whilst nickel monoxide with the negative quantity of -1300 units remains unaltered.

Nickel and cobalt decompose water—they dissolve in dilute acids with evolution of hydrogen. In this respect they stand between cadmium and tin, as is shown by the evolution of heat on decomposition of dilute hydrochloric acid by these metals thus:—

Zinc . . .	34.20 heat-units.
Iron . . .	21.31 "
Cadmium . . .	17.61 "
Cobalt . . .	16.18 "
Nickel . . .	15.06 "
Tin . . .	2.5 "

The following table gives the thermal values determined for cobalt and nickel in various reactions. Ni and Co = 59. Temperature = 18°:—

Reaction	Evolution of Heat	Explanation
Co, Cl ² . . .	+ 76.48 heat-units.	Anhydrous chloride
Co, O, H ² O . . .	63.4 "	} Monoxide and hydrated oxide from metal, oxygen, and water
Co ² , O ³ , 3H ² O . . .	149.3 "	
Co, O ² SO ² , 7H ² O . . .	162.97 "	Crystallised sulphate
2CoO ² H ² , O, H ² O . . .	22.5 "	Oxidation of monoxide to sesquioxide
2CoO ² H ² , O, H ² O . . .	- 0.7 "	Further oxidation of sesquioxide
CoO ² H ² , 2HClAq. . .	+ 21.14 "	} Heat of neutralisation of monoxide
CoO ² H ² , SO ³ Aq. . .	24.67 "	
CoCl ² , Aq. . .	18.34 "	} Heat of solution of anhydrous chloride and crystallised sulphate
CoSO ⁴ , 7H ² O Aq. . .	- 3.57 "	
Co.Cl ² , Aq. . .	+ 94.82 "	} Formation of chloride and sulphate in aqueous solution
Co, O, SO ³ Aq. . .	88.07 "	
Ni, Cl ² . . .	74.53 "	Anhydrous chloride
Ni, O, H ² O . . .	60.84 "	} Monoxide and sesquioxide
Ni ² , O ³ , 3H ² O . . .	120.38 "	
Ni ² , O ² , SO ² , 7H ² O . . .	162.53 "	Crystallised sulphate
2NiO ² H ² , O, H ² O . . .	- 1.3 "	Oxidation of monoxide to sesquioxide
NiO ² H ² , 2HClAq. . .	+ 22.58 "	} Heat of neutralisation
NiO ² H ² , SO ³ Aq. . .	26.11 "	
NiCl ² , Aq. . .	19.17 "	} Heat of solution of anhydrous chloride and crystallised sulphate
NiSO ⁴ , 7H ² O Aq. . .	- 4.25 "	
Ni, Cl ² , Aq. . .	+ 93.7 "	} Formation of chloride and sulphate in aqueous solution
Ni, O, SO ³ Aq. . .	86.95 "	

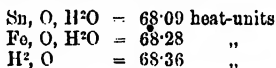
3. Tin Compounds (Thomsen, *loc. cit.*) Sn = 118. Temperature 81°.*Evolution of Heat on Solution of Compounds in Water.*

Reaction	Evolution of Heat	Explanation
$\text{SnCl}_4, \text{Aq.}$	29.92 heat-units.	Anhydrous tetrachloride
$\text{SnCl}_4\text{K}_2, \text{Aq.}$	-3.38	Chloride of tin and potassium
$\text{SnCl}_2, \text{Aq.}$	+ .35	Anhydrous dichloride
$\text{SnCl}_2, 2\text{H}_2\text{O}, \text{Aq.}$	-5.37	Crystalline hydrated dichloride

Heat of Formation of the Chlorides and Oxides of Tin.

Reaction	Evolution of Heat	Explanation
Sn, Cl_2	80.79 heat-units	Formation of anhydrous chlorides from metal and chlorine
Sn, Cl_4	127.24	
$\text{Sn}, \text{O}, \text{H}_2\text{O}$	68.09	Formation of hydrates from metal, oxygen, and water
$\text{Sn}, \text{O}_2, 2\text{H}_2\text{O}$	133.49	
$\text{SnCl}_2, 2\text{H}_2\text{O}$	5.72	Crystalline hydrated dichloride
$\text{SnCl}_4, 2\text{KCl}$	24.16	Crystalline chloride of tin and potassium
$\text{SnO}_2\text{H}_2, 2\text{HClAq.}$	2.77	Heat of neutralisation of oxides for hydrochloric acid
$\text{SnO}_2\text{H}_4, 4\text{HClAq.}$	3.11	
$\text{SnO}_2\text{H}_2, 2\text{NaOHAq.}$	215	Heat of neutralisation of oxides for sodium hydrate
$\text{SnO}_2\text{H}_4, 4\text{NaOHAq.}$	9.56	
$\text{SnCl}_2, \text{Aq.}$	81.14	Aqueous solutions of chlorides from metal, chlorine, and water
$\text{SnCl}_4, \text{Aq.}$	157.16	
$\text{SnCl}_4\text{Aq}, 2\text{KClAq.}$	-250	Reaction of tin tetrachloride on potassium chloride in aqueous solution.

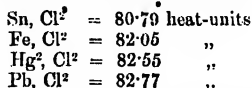
The affinity of tin for both oxygen and chlorine is very great, but more so for the latter than the former body. The formation of the hydrated oxide of tin from the metal, oxygen and water is accompanied by the same evolution of heat as the formation of hydrated monoxide of iron, and of water thus:—



The affinity of tin for oxygen is 2.41 heat-units greater than that of cadmium, but 14.59 less than that of zinc.

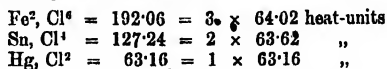
Tin readily takes up another atom of oxygen, and the oxidation of the hydrated monoxide into the hydrated dioxide is accompanied by an evolution of 65.4 heat-units.

The heat of neutralisation of the monoxide of tin for hydrochloric acid is 2.77 heat-units, that of the dioxide for soda 9.56 heat-units. Hence tin does not readily decompose water either in weakly acid or in alkaline solutions. The reduction of water by tin and very dilute hydrochloric acid gives only 2.5 heat-units; but the evolution of heat and rapidity of decomposition increase with the degree of concentration of the acid. This is the reason why tin is a suitable reducing agent for many organic bodies, since the oxidation of the tin takes place at the cost of the more easily reducible body. The heat of formation of the anhydrous stannous chloride is almost the same as that of ferrous chloride, mercurous chloride, and lead chloride.



On the other hand the behaviour of these chlorine-compounds to water is very different, the evolution of heat on solution of stannous chloride being +0.35 units, ferrous chloride +17.9 units, lead chloride -6.8 units; that of mercurous chloride is unknown.

A comparison of the higher chlorides of these metals gives—



But as the numbers of chlorine-molecules in the compounds are as 3 : 2 : 1, it follows that the formation of ferric, stannic, and mercuric chlorides is accompanied by an equal evolution of heat for equal quantities of chlorine. The lower chlorides therefore of iron, tin, and mercury are formed with evolution of the same quantity of heat,

amounting in the mean to 81·8 units for each molecule of chlorine, and the higher chlorides also evolve equal quantities, of heat, amounting to 63·6 units for each molecule of chlorine. It may therefore be supposed that the union of the chlorine atoms in the higher chloride is of a similar nature, and that the higher chloride is not made up of the lower chloride and chlorine.

The difference of these values viz., $81\cdot8 - 63\cdot6 = 18\cdot2$ units, is the quantity, which Thomsen has often pointed to as the thermo-chemical constant.

Again, $81\cdot8 = 9 \times 9\cdot089$
 $63\cdot6 = 7 \times 9\cdot086$,

thus the absolute evolution of heat for chlorine in the two groups shows the same constant for the half of $18\cdot0 = 2 \times 9\cdot1$.

Whether other metals which have more than one chloride exhibit the same relation is not known, since those of copper only have been investigated.

The evolution of heat for cuprous chloride is 65·75, for cupric chloride 51·63 heat-units for each molecule of chlorine: the absolute evolution of heat is therefore considerably less than in the above cases; but—

$$81\cdot8 : 63\cdot6 = 1\cdot286 : 1$$

$$65\cdot7 : 51\cdot63 = 1\cdot274 : 1,$$

and therefore the evolution of heat of cuprous and cupric chloride stands in the same relation as those of the lower and higher chlorides of tin, iron, and mercury.

4. Platinum and Palladium Compounds (Thomsen, *J. pr. Chem.* [2], xv. 435, 473).

(a.) Heat of Formation of the Haloid Double Salts of Platinum.

Reaction	Heat evolved	Explanation
Pt, Cl ⁴ , 2KCl . . .	89·5 units	Anhydrous salts corresponding with the chlorido and bromide.
Pt, Br ⁴ , 2KBr . . .	59·26 "	
Pt, Cl ⁴ , 2NaCl . . .	73·72 "	
Pt, Br ⁴ , 2NaBr . . .	46·79 "	Hydrated sodium-platinum chloride and bromide.
Pt, Cl ⁴ , 2NaCl, 6H ² O . . .	92·89 "	
Pt, Br ⁴ , 2NaBr, 6H ² O . . .	95·33 "	
Pt, Cl ² , 2KCl . . .	45·17 "	Salts corresponding with the chloride and bromide.
Pt, Cl ² , 2AmCl . . .	42·55 "	
Pt, Br ² , 2KBr . . .	32·31 "	

(b.) Heat of Solution of the Double Haloid Salts.

Reaction	Heat evolved	Explanation
PtCl ⁶ K ² . . .	— 13·76 units	From these numbers may be deduced the evolution of heat on addition of 6 mols. of water of crystallisation.
PtBr ⁶ K ² . . .	— 12·26 "	
PtCl ⁶ Na ² . . .	+ 8·54 "	
PtBr ⁶ Na ² . . .	+ 9·99 "	
PtCl ⁶ Na ² .6H ² O . . .	— 10·63 "	
PtBr ⁶ Na ² .6H ² O . . .	— 8·55 "	PtCl ⁶ Na ² .6H ² O = 19·17. PtBr ⁶ Na ² .6H ² O = 18·54.
PtCl ⁴ K ² . . .	— 12·22 "	
PtCl ⁴ Am ² . . .	— 8·48 "	
PtBr ⁴ K ² . . .	— 10·63 "	

(c.) Reactions in the Wet Way.

Reaction	Heat evolved	Explanation
Pt, Cl ⁴ , 2RClAq . . .	84·62 units	H ² , K ² , Na ² , Am ² , or an atom of the metals of the alkaline earths or of the magnesium series, may be substituted for 2R without any alteration in the evolution of heat.
Pt, Br ⁴ , 2RBrAq . . .	57·16 "	
Pt, Cl ² , 2RClAq . . .	41·38 "	
Pt, Br ² , 2RBrAq . . .	31·44 "	
Pt, O ² , 6HClAq . . .	64·06 "	A molecule of hydrogen may be replaced by two equivalents of the metals named without altering the evolution of heat.
Pt, O ² , 6HBrAq . . .	80·36 "	
Pt, O, 4HClAq . . .	31·55 "	
Pt, O, 4HBrAq . . .	43·44 "	
Pd, Cl ⁴ , 2KCl . . .	79·06 "	Heat of formation of the double chlorides, the iodide, and the hydrated oxides of palladium.
Pd, Cl ² , 2KCl . . .	52·67 "	
Pd, I ² , H ² O . . .	18·18 "	
Pd, O ² , 2H ² O . . .	30·43 "	
Pd, O, H ² O . . .	22·71 "	

Palladium-compounds.

Reaction	Heat evolved	Explanation
$\text{PdCl}^2\text{K}^2, \text{Aq}$	15.00? units	Heat of solution of the double chlorides.
$\text{PdCl}^2\text{K}^2, \text{Aq}$	13.63 "	
$\text{Pt}, \text{Cl}^2, 2\text{HClAq}$	72.94 ? "	
$\text{Pd}, \text{Cl}^2, 2\text{HClAq}$	47.92 "	Formation of the chloro-palladium hydrogen acids in aqueous solution.
$\text{Pd}, \text{O}^2, 6\text{HClAq}$	52.38 ? "	
$\text{Pd}, \text{O}, 4\text{HClAq}$	37.64 "	
$\text{PdO}^2\text{H}^2, 6\text{HClAq}$	21.95 ? "	Evolution of heat on solution of the hydrates in hydrochloric acid.
$\text{PdO}^2\text{H}^2, 4\text{HClAq}$	14.93 "	

Temperature 18° . Pt. = 198. Pd. = 106.

The haloïd compounds of platinum and palladium form with the hydrogen compounds of chlorine, bromine, and iodine, compounds which are soluble in water, and exhibit the character of bibasic hydracids, *i.e.* they form crystalline soluble salts with the alkalis, alkaline earths, and bases of the magnesium series, and more or less insoluble salts with the oxide of lead, mercury, and silver. The isomorphism of several of these groups indicates similarity of constitution, and the heat of neutralisation for the same base is the same as that of hydrochloric acid. The formulæ of the two series of acids are PtCl^2H^2 and PtCl^2H^2 . Tin, mercury, and gold form similar acids, and if the compounds of fluorine were included, silicon and several other elements would be added to the group. The heat of neutralisation of all these acids agrees with that of hydrochloric acid. These bodies are not known in the anhydrous state, but several of them have been obtained as hydrated crystalline acids, *e.g.* $\text{PtCl}^2\text{H}^2 + 6\text{H}^2\text{O}$, $\text{AuCl}^2\text{H}^2 + 3\text{H}^2\text{O}$, $\text{AuBr}^2\text{H}^2 + 5\text{H}^2\text{O}$, $\text{HgBr}^2\text{H}^2 + 4\text{H}^2\text{O}$. They are all decomposed by heat, and yield normally water, haloïd acids, and a haloïd compound of the metal; but in many cases the temperature rises so high that the metallic compound is partially decomposed. Some of these acids are decomposed by water, while others possess considerable stability.

It appears to be a general rule that the heat of solution of potassium salts is always more strongly negative than that of the corresponding sodium salts, and that the differences of the heats of solution of the corresponding haloïd salts of potassium and sodium are simple multiples of a constant. Thus:

	Units
$\text{K}^2\text{Cl}^2, \text{Aq} - \text{Na}^2\text{Cl}^2, \text{Aq}$	$8.88 + 2.36 = 6.52 = -2 \times 3.26$
$\text{K}^2\text{Br}^2, \text{Aq} - \text{Na}^2\text{Br}^2, \text{Aq}$	$10.16 + 38 = 9.78 = -3 \times 3.26$
$\text{K}^2\text{I}^2, \text{Aq} - \text{Na}^2\text{I}^2, \text{Aq}$	$10.22 - 2.44 = 12.66 = -4 \times 3.165$
$\text{PtCl}^2\text{K}^2, \text{Aq} - \text{PtCl}^2\text{Na}^2, \text{Aq}$	$13.76 - 8.54 = 22.30 = -7 \times 3.186$
$\text{PtBr}^2\text{K}^2, \text{Aq} - \text{PtBr}^2\text{Na}^2, \text{Aq}$	$12.26 - 9.99 = 22.25 = -7 \times 3.179$

The explanation of this fact is that the sodium salts are not fully saturated compounds like the potassium salts; they have a tendency to combine with water, and this tendency is least with sodium chloride, greatest with the haloïd compounds of sodium and platinum. The formation of potassium-palladium chloride is accompanied by a greater evolution of heat than that of potassium-platinum chloride, while, on the other hand, it is just the reverse in the case of the dichlorides. This would follow from the fact that palladium forms the dichloride, platinum the tetrachloride most readily. The heat evolved in each case is as follows:

	Platinum	Palladium
Dichloride	4517 units	2×26.335 units
Tetrachloride	2.4475 "	3×26.353 "

More important is the result of the comparison of the difference of evolution of heat in the formation of compounds of two different stages of the same metals. Thus in the passage of the compounds of gold, mercury, palladium, and platinum from a lower to a higher stage by addition of a molecule of chlorine, bromine, and iodine, the evolution of heat is as follows:

	Chlorine	Bromine	Iodine
Mercury	6×8.858	4×8.822	3×8.793
Platinum	5×8.866	3×8.983	—
Palladium	3×8.797	—	—
Gold	2×8.505	1×8.930	—

A molecule of chlorine, therefore, gives in these allied reactions an unequal evolution of heat in the proportion of 2 : 3 : 5 : 6, bromine of 1 : 3 : 4, &c. The mean constant is the same in all, *viz.* 8.850 units.

4. Gold-compounds (Thomsen, *J. pr. Chem.* [2], xiii. 348-369). Gold shows allotropic peculiarities according to the kind of solution from which it is precipitated, and the kind of reagent used. Three such modifications have been investigated. When gold is precipitated from a solution of auric chloride by sulphurous acid, it forms a mass which boils together; when precipitated in a similar manner from a solution of the bromide, it forms a very fine dark powder, which retains its pulverulent state even on drying: when reduced from the sub-chloride, sub-bromide, or sub-iodide by sulphurous acid or a hydrogen acid, it has the form of a very fine powder with perfect metallic lustre and a yellow colour. These modifications differ from each other by unequal evolution of heat in similar reactions. The gold which has been precipitated from the chloride by sulphurous acid shows least energy and is taken as the standard of reference. The energy of gold precipitated from the bromide is greater by an amount represented by 3.2 heat-units, while that of gold precipitated from the sub-chloride, the sub-bromide, or sub-iodide is 4.7 units greater for each atom. The last two modifications, therefore, evolve respectively 3.2 and 4.7 units of heat when converted into the first modification.

The following tables give the direct results of the experiments on the thermochemistry of the gold compounds:

Reaction	Evolution of heat	Explanation
(AuCl ³ Aq, HClAq) . . .	4.53 units	Reactions of halogen-acids on the soluble haloïd compounds of gold.
(AuBr ³ Aq, HBrAq) . . .	7.7 "	
(AuCl ³ Aq, 3HBrAq) . . .	15.21 "	
(AuBr ³ Aq, 3HClAq) . . .	4.28 "	
(AuCl ³ HAq, 4HBrAq) . . .	13.8 "	
(AuBr ³ HAq, HClAq) . . .	— .51 "	Heat of neutralisation of hydrated oxide for hydrobromic and hydrochloric acids.
(AuO ³ H ³ , 4HBrAq) . . .	36.78 "	
(AuO ³ H ³ , 4HClAq) . . .	22.97 "	Reduction of soluble haloïd compounds by sulphurous acid.
(AuCl ³ Aq, 2SO ² Aq) . . .	83.6 "	
(AuBr ³ HAq, 2SO ² Aq) . . .	61.79 "	Decomposition of sub-chloride and sub-bromide by the corresponding halogen acid.
(3AuCl, HClAq) . . .	4.98 "	
(3AuBr, HBrAq) . . .	3.65 "	Reduction of sub-bromide and sub-iodide by sulphurous acid.
(2AuBr, SO ² Aq) . . .	42.76 "	
(2AuI, SO ² Aq) . . .	23.4 "	Neutral chloride decomposed by KI.
(AuCl ³ Aq, 3KIAq) . . .	45.66 "	
(AuBr ³ II, 5H ² O, Aq) . . .	— 11.4 "	Direct determination of heat of solution.
(AuCl ³ Aq) . . .	+ 4.45 "	
(AuBr ³ , Aq) . . .	— 3.71 "	
(AuBr ³ II BrAq) . . .	+ 3.88 "	Indirect determination of the same for AuBr ³ .

From these data Thomsen calculates the following values of the quantities of heat evolved in the formation of gold-compounds, all the values relating to that modification of gold which is precipitated from a dilute solution of the chloride by sulphurous acid.

Reaction	Evolution of heat	Explanation
(Au, Cl ³) . . .	22.82 heat-units	Heat of formation of anhydrous haloïd compounds.
(Au, Br ³) . . .	8.85 "	
(Au, Cl) . . .	5.81 "	
(Au, Br) . . .	— .08 "	
(Au, I) . . .	— 5.62 "	Heat of formation of hydrated oxide.
(Au ² , O ³ , H ² O) . . .	— 13.19 "	
(AuCl ³ , Aq) . . .	+ 4.45 "	Heat of solution.
(AuBr ³ , Aq) . . .	— 3.76 "	
(AuBr ³ II, 5H ² O, Aq) . . .	— 11.40 "	
(AuO ³ H ³ , 3HBrAq) . . .	29.18 "	Heat of neutralisation of hydrated oxide for 3 and 4 mols. of halogen acids.
(AuO ³ H ³ , 3HClAq) . . .	18.44 "	
(AuO ³ II ³ , 4HBrAq) . . .	36.78 "	
(AuO ³ II ³ , 4HClAq) . . .	22.97 "	Heat of formation of solutions of neutral haloïd compounds.
(Au, Cl ³ , Aq) . . .	27.27 "	
(Au, Br ³ , Aq) . . .	5.09 "	Heat of formation of solutions of acid haloïd compounds.
(Au, Cl ³ , HClAq) . . .	31.80 "	
(Au, Br ³ , HBrAq) . . .	12.79 "	

Heat of Formation of the Carbon-, Boron-, and Silicon-compounds of Iron and Manganese (Troost & Hautefeuille, *Ann. Chim. Phys.* [5], ix. 56-70).

The combination of iron and carbon is attended with absorption of heat, as shown by the fact that when a carbide of iron is chlorinated by treating it with mercuric chloride, the quantity of heat evolved increases with the proportion of carbon present: thus:

1 gram of iron containing only traces of carbon gave	0.827 heat-units
1 " " " 2.8 per cent. " "	0.879 "
1 " " " 4.0 " " "	0.896 "

The carbide of iron must be regarded therefore not as a true chemical compound, but as a solution of the carbon in the iron.

The formation of manganese carbide, on the other hand, is attended with evolution of heat as shown by the fact that a specimen containing 4.8 per cent. carbon gave, when treated with mercuric chloride, 1.19 heat-units, whilst another containing 5.8 per cent. carbon gave only 1.01. The carbides of manganese are therefore true chemical compounds; the compound Mn^2C has, indeed, a degree of stability comparable with that of the most stable inorganic compounds. The 'ferro-manganeses' of commerce, Mn^2Fe^3 , Mn^2Fe , Mn^2Fe , &c., are likewise true chemical compounds, their formation being attended with disengagement of heat.

Silicide of manganese is formed with great evolution of heat. In the combination of silicon with iron, the evolution of heat is next to nothing for the proportion of silicon which is found in metallurgic products.

The heat of formation of crystallised manganese boride, MnB^2 , from its elements amounts to 2.487 heat-units for 1 gram. The quantities of heat evolved in the formation of iron boride, containing 11 and 23 per cent. boron, are respectively 0.517 and 1.611 units for 1 gram.

Phosphide of iron is formed with great evolution of heat. Sulphide of iron is probably formed with scarcely perceptible evolution of heat. The formation of sulphide and phosphide of manganese from the carbide is also attended with great evolution of heat.

Heat evolved in the transformations of Acetylene (Berthelot, *Ann. Chim. Phys.* [5], ix. 165-174):

C^2H^2 gas + O^5 gas = $2CO^2$ gas + H^2O liquid	321.0
C^2H^2 + O^4 = $C^2H^2O^4$, Oxalic acid, solid	260.8
C^2H^2 + O + H^2O = $C^2H^4O^2$, Acetic acid, cryst.	113.5
C^2H^2 + O^4 = CH^2O^2 , Formic acid, cryst. + CO^2 gas	253.5
C^2H^2 + H^2 = C^2H^4 , Ethylene	56.0
C^2H^2 + N^2 = $2CNH$, Hydrogen Cyanide, gas	36.0
$3C^2H^2$ = C^3H^6 , Benzene, liquid	nearly 190.0
C^2 , diamond + H^2 = C^2H^2 gas	64.0

Heats of Combination of Ethylene (Berthelot, *ibid.* 296, 306):

C^2H^4 gas + Br^2 liquid = $C^2H^4Br^2$ liquid	+ 29.3
C^2H^4 " + Br^2 gas = $C^2H^4Br^2$ "	36.5
C^2H^4 " + Br^2 " = $C^2H^4Br^2$ gas	about 28.0
C^2H^4 " + H^2SO^4 dilute = $C^2H^4.H^2O.SO^4$, Iscthionic acid, dil.	16.01
C^2H^4 " + SO^3 solid + water = $C^2H^4.H^2O.SO^4$, " "	53.3

Heat of Formation of Ethyl Chloride and Iodide on the assumption that the ethers of ethylene give the same numbers as those of amylene (*infra*) (Berthelot, *ibid.* 348):

C^2H^4O gas + HCl gas = C^2H^5Cl gas + H^2O gas	- 2.7
C^2H^4O " + HI " = C^2H^5I " + H^2O "	- 1.3

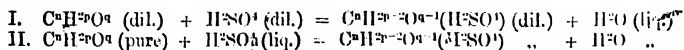
If the haloïd acid alone were gaseous, the value for C^2H^5Cl would be 3.4, and for C^2H^5I , 6.0; if, on the other hand, all the acting substances were dissolved in water, the value for C^2H^5Cl would be -16.6, and for C^2H^5I -16.0, the ethers being insoluble in water.

Heat of Combination of Amylene with the Haloïd Acids (Berthelot, *ibid.* 292):

C^3H^{10} liquid + HI (sp. gr. 1.98)	1.7
C^3H^{10} " + HBr (sp. gr. 1.79)	0.8
C^3H^{10} " + HCl (" 1.20)	0.95
C^3H^{10} " + HI gas	17.6
C^3H^{10} " + HBr gas	15.2
C^3H^{10} " + HCl "	14.8
C^3H^{10} gas + HI " = $C^3H^{10}.HI$ liquid	22.9
C^3H^{10} " + HBr " = $C^3H^{10}.HBr$	20.5
C^3H^{10} " + HCl " = $C^3H^{10}.HCl$	20.0

The heat of evaporation of amylene at 12.5° in a current of air was found to be -5.25.

Heat of Conversion of Alcohols into Acid Alcoholic Sulphates (Berthelot, *ibid.* 307). The reactions are :



		I	II
Methyl Alcohol	CH^3O	-5.1	+13.8
Ethyl Alcohol	C^2H^6O	4.7	11.7
Propyl Alcohol	C^3H^8O	4.05	15.9
Pseudopropyl Alcohol	C^3H^8O	3.3	17.1
Isobutyl Alcohol	$C^4H^{10}O$	2.2	17.6
Amyl Alcohol (ferment.)	$C^5H^{12}O$	0.2	19.5
Glycerin *	$C^3H^8O^3$	3.2	15.2

Heat of Formation and of various reactions of Aldehyde (Berthelot, *Ann. Chim. Phys.* [5], ix, 174-180):

C^2H^4O pure + O = $C^2H^4O^2$, Acetic acid, liquid	+ 70.1
C^2H^4O " + O = $C^2H^4O^2$ " solid	+ 67.6
C^2H^4O gas + O = $C^2H^4O^2$ " gas	- 70.0
C^2H^4O liq. + H^2 = C^2H^6O liq. . . . + 28.0; all gas	+ 32.0
C^2H^4O gas + H^2 = C^2H^6 gas + H^2O	+ 37.0
C^2H^4O " = CH^4 + CO	- 5.5
C^2H^4O " = CH^2 + H^2O	- 45.0

The last two reactions are brought about by heat, therefore by foreign energy.

$C^2H^4O + Cl^2 = C^2H^4ClO + HCl$	+ 39.5	
$C^2H^4O + Br^2 = C^2H^4BrO + HBr$	+ 16.0; Br^2 gas	+ 23.0
$C^2H^4O + I^2 = C^2H^4IO + HI$	- 9.8; I^2 "	- 8.0

The negative value for the iodine-compound is in accordance with the impossibility of producing the compound by direct action.

C^2H^4O gas = CH^4 + CO^2	- 5.5
C^2H^4O " = C^2H^2 + H^2O	- 45.0
C^2 diamond + H^4 + O = C^2H^4O liq. . . . + 46.0; gas	+ 40.0
C^2H^4 ethylene + O = C^2H^4O gas	+ 48.0
C^2H^6O alcohol, gas = C^2H^4O " + H^2	about - 24.0
C^2H^4O " " + O = C^2H^4O " + H^2O liquid	+ 35.0
C^2H^4O " liq. + O = C^2H^4O liq. + H^2O "	+ 41.0
$C^2H^4O^2$ acetic acid gas + H^2 = C^2H^4O gas + H^2O gas =	- 11.0

The last mentioned reaction cannot be performed directly.

The heat of vaporisation of aldehyde at ordinary temperature is on the average -60.0.

Normal Propyl Aldehyde (Berthelot, *Compt. rend.* lxxxiii. 413):

C^3 (diamond) + H^6 + O = C^3H^8O liquid	69.6
C^3H^8O (propyl alcohol) + O = $C^3H^8O^2$ + H^2O	56.6
C^3H^6 (propylene) gas + O = C^3H^8O { liquid	72.5
	{ gas about 66.0
C^3H^8O dissolved + O gas = $C^3H^8O^2$, dissolved at 23°	70.3
C^3H^8O pure + 840 H^2O at 23°	4.0
$C^3H^8O^2$ propionic acid, liquid, + Water	0.5
C^3H^8O , pure + O = $C^3H^8O^2$, Propionic acid, pure	74.0

Acetone (Berthelot, *ibid.* 414):

C^3 (diamond) + H^6 + O = C^3H^6O , liquid	65.0
C^3H^6 gas + O = C^3H^6O "	68.5
Heat of combustion	424.0

Heat of Formation of Ethyl Acetate (Berthelot, *Ann. Chim. Phys.* [5], ix. 342).

* The calculation for glycerin was made according to the weight of sulphuric acid neutralised, without enquiry as to the possible formation of two or more compounds.

$\text{C}^2\text{H}^3\text{ClO}$ pure + $\text{C}^2\text{H}^6\text{O}$ diss. = $\text{C}^2\text{H}^3(\text{C}^2\text{H}^3\text{O}^2)$ diss. + HCl diss.	+ 21.52
$\text{C}^2\text{H}^3\text{O}^2$ diss. + $\text{C}^2\text{H}^6\text{O}$ „ = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ „ + H^2O	- 1.8
$\text{C}^2\text{H}^3\text{O}^2$ liq., pure + $\text{C}^2\text{H}^6\text{O}$ pure = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ pure + H^2O liq.	- 2.0
$\text{C}^2\text{H}^3\text{O}^2$ solid + $\text{C}^2\text{H}^6\text{O}$ liq. = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ liq. + H^2O solid	- 1.0
$\text{C}^2\text{H}^3\text{O}^2$ gas + $\text{C}^2\text{H}^6\text{O}$ gas = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ gas + H^2O gas	- 6.6

For the theoretical formation from ethylene :

C^2H^4 gas + $\text{C}^2\text{H}^4\text{O}^2$ gas ^c = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ gas	+ 10.1
C^2H^4 „ + $\text{C}^2\text{H}^4\text{O}^2$ „ = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ liquid	+ 21.0

For various modes of formation by double decomposition, calculation gives :

$\text{C}^2\text{H}^3\text{NaSO}^1$ + $\text{C}^2\text{H}^3\text{NaO}^2$ = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ liq.* + Na^2SO^1	+ 8.3	
$\text{C}^2\text{H}^3\text{Cl}$ liq. + $\text{C}^2\text{H}^3\text{NaO}^2$ = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ liq. + NaCl	+ 17.2	Ether gaseous
$\text{C}^2\text{H}^3\text{I}$ „ + $\text{C}^2\text{H}^3\text{AgO}^2$ = $\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ „ + AgI	+ 44.2	+ 12.8
		+ 38.8
		Heat of solution
$\text{C}^2\text{H}^3.\text{C}^2\text{H}^3\text{O}^2$ + 60 parts water at 15°		+ 3.06
This gives for the solution of the gas		+ 14.00

Heat of Formation of the Nitric Ethers of Ethyl Alcohol, Glycerin, and Mannite (Berthelot, *Compt. rend.* lxxxii. 361).

$\text{C}^2\text{H}^6\text{O}$ pure + NO^3H pure = $\text{C}^2\text{H}^3\text{NO}^3$ pure + H^2O liq.	+ 5.8
$\text{C}^2\text{H}^6\text{O}$ dissolved + NO^3H dissolved = $\text{C}^2\text{H}^3\text{NO}^3$ dissolved + Water	- 3.0
$\text{C}^2\text{H}^6\text{O}^3$ + $3\text{NO}^3\text{H}$ = $\text{C}^2\text{H}^3(\text{NO}^3)^3$ + $2\text{H}^2\text{O}$	+ 13.0
$\text{C}^2\text{H}^6\text{O}^3$ diss. + $3\text{NO}^3\text{H}$ dil. = $\text{C}^2\text{H}^3(\text{NO}^3)^3$ pure + Water	- 10.0
$\text{C}^2\text{H}^6\text{O}^3$ pure + $6\text{NO}^3\text{H}$ = $\text{C}^2\text{H}^3(\text{NO}^3)^6$ + $6\text{H}^2\text{O}$	+ 21.2
$\text{C}^2\text{H}^6\text{O}^3$ diss. + $6\text{NO}^3\text{H}$ dil. = $\text{C}^2\text{H}^3(\text{NO}^3)^6$ + $6\text{H}^2\text{O}$	- 17.1
		Heat of solution
$\text{C}^2\text{H}^3(\text{NO}^3)$ + 180 parts by weight of water at 16°	+ 0.99

Heat of Formation and Combustion of Explosive Nitro-compounds (Berthelot, *Ann. Chim. Phys.* [5], ix. 161-165).

1. *Evolution of Heat in the Formation of Nitro-derivatives from their Elements.*

	Equivalent	Heat evolved	
		1 eq.	1 gram
Ethyl Nitrate, $\text{C}^2\text{H}^3\text{NO}^3$	91 grams	+ 31	+ 0.341
Nitroglycerin, $\text{C}^3\text{H}_5(\text{NO}^3)_3\text{O}^3$	227 „	+ 25	+ 0.110
Gun-cotton,* $\text{C}^6\text{H}_7(\text{NO}^3)_3\text{O}^3$	297 „	+ 273	+ 0.919
Pieric acid, $\text{C}^6\text{H}_2(\text{NO}^3)_3\text{O}$	229 „	- 14	- 0.067
Potassium Pierate, $\text{C}^6\text{H}_2\text{K}(\text{NO}^3)_3\text{O}$	267 „	+ 51	+ 0.186
Nitric acid, NO^3H	63 „	+ 19	+ 0.316
Potassium Nitrate, NO^3K	101 „	+ 97.3	+ 0.926

The evolution of heat in the decomposition of explosive bodies—the water being considered as gaseous—can be calculated only for nitroglycerin, which alone contains sufficient oxygen for its combustion. This, for 1 mol. = 227 grams, amounts to 405.5, and for 1 gram to 1.786 kil.-degrees.

2. *Evolution of Heat in the Perfect Combustion of Explosive Substances by free Oxygen, the water being supposed to be gaseous.*

	Molecule	Heat of combustion	
		1 mol.	1 gram
Ethyl Nitrate	91	305.5	3.357
Nitroglycerin	227	406.5	1.786
Gun-cotton	297	—	1.572
Pieric acid	229	668.0	2.919
Potassium Pierate	267	661.0	2.473

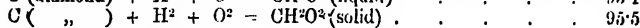
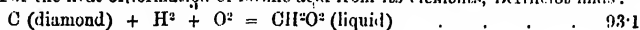
If A denotes the heat evolved in the combustion of 1 equivalent (semi-molecule) of the substance containing carbon and hydrogen by free oxygen, and n the number of equivalents of oxygen consumed, the heat evolved when the combustion is effected by various oxidising agents is as follows :

* Berthelot gives for gun-cotton the formula $\text{C}^6\text{H}_7\text{O}^3(\text{NO}^3\text{H})^3$, and molecular weight 549, making the heat of formation for 1 mol. 502; but there is an error in the calculation: the molecular weight of $\text{C}^6\text{H}_7\text{O}^3(\text{NO}^3\text{H})^3$ is 351, and the corresponding heat-equivalent is 322 (or 273 for mol. wt. 297).

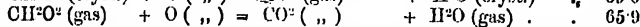
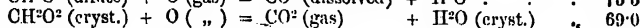
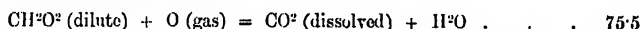
Copper Oxide, $n \frac{\text{CuO}}{2}$	A - 18.6n
Lead Oxide, $n \frac{\text{PbO}}{2}$	A - 25.1n
Tin Oxides $\left\{ n \frac{\text{SnO}}{2} \right.$ $\left. n \frac{\text{SnO}_2}{2} \right\}$	A - 35.0n
Antimony Tetroxide, $n \frac{\text{Sb}_2\text{O}_4}{2}$	A - 31.0n
Mercuric Oxide, $n \frac{\text{HgO}}{2}$	A - 15.3n
Bismuth Oxide, $n \frac{\text{Bi}_2\text{O}_3}{2}$	A - 6.6n
Silver Oxide, $n \frac{\text{Ag}_2\text{O}}{3}$	A - 3.0n
Lead Nitrate, $n \frac{\text{Pb}(\text{NO}_3)_2}{12}$	A - 5.3n
Silver Nitrate, $n \frac{\text{AgNO}_3}{6}$	A - 1.1n
Potassium Nitrate, $n \frac{\text{KNO}_3}{6}$	A - 1.9n $\left\{ \begin{array}{l} \text{formation} \\ \text{of } \text{K}_2\text{CO}_3 \end{array} \right.$
Potassium Chlorate, $n \frac{\text{KClO}_3}{6}$	A - 2.5n

Heat evolved in the Formation and Combustion of Formic and Oxalic Acid (Berthelot, *Compt. rend.* lxxvi. 1433-1441; *Ann. Chim. Phys.* [5], v. 310-318).

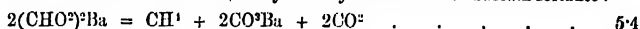
For the heat of formation of formic acid from its elements, Berthelot finds:



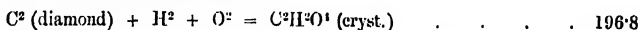
For the heat of combustion:



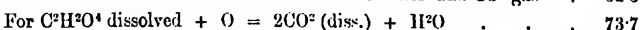
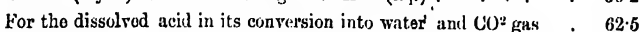
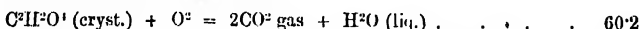
For the formation of marsh gas by the dry distillation of barium formate:



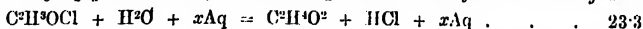
For the formation of oxalic acid:



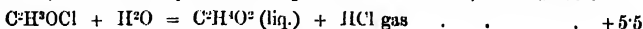
For the combustion of oxalic acid:



Thermochemistry of Acetyl-derivatives (Berthelot a. Louguine (*Ann. Chim. Phys.* [5], vi. 289-304). The decomposition of acetyl chloride by water:



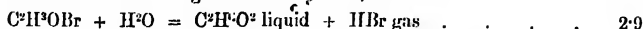
Since now the heat of solution of gaseous hydrochloric acid in water amounts to 17.4 heat-units, and that of crystallisable liquid acetic acid to 0.4, it follows that



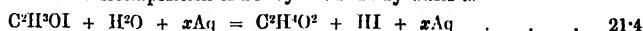
The decomposition of acetyl bromide by water gives



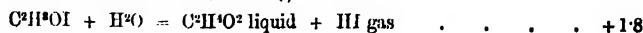
The heat of solution of gaseous HBr is 20.9, therefore



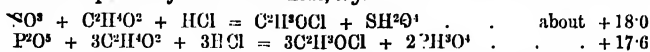
The heat of decomposition of acetyl iodide by water is



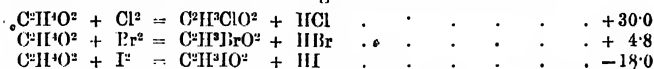
The heat of solution of HI is 19.57, therefore:



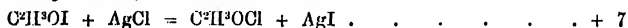
According to these results, the formation of the acid chlorides, bromides, and iodides from the corresponding organic acids and the halogen acids should be attended with absorption of heat. Consequently, these bodies are formed only in presence of a compound, like phosphoric or sulphuric anhydride, the combination of which with water is accompanied by evolution of heat, *e.g.*



Hence for the substitution of the halogen-elements in acetic acid :



It follows from this that the direct substitution of iodine for hydrogen cannot be effected. On the other hand, acetyl iodide and iodated compounds in general are easily attacked by hydriodic acid, with separation of iodine. Acetyl chloride is converted by gaseous hydriodic acid into iodide, and by gaseous hydrobromic acid into bromide, with evolution of 3 kil.-degrees of heat. On the other hand, chlorine expels bromine from acetyl bromide, and iodine from the iodide. Moreover, iodine can be replaced by chlorine, with the aid of silver chloride :



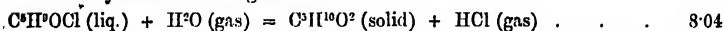
These examples show how thermochemical investigations may serve as guides in the choice of reagents for the preparation of any desired compound.

The decomposition of the *chlorides* and *bromides* of the *fatty acid radicals* by *water* has also been studied by W. Louguine. The following values relate to the reaction :

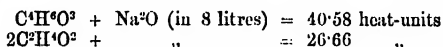
Chloride or Bromide (liquid) + H²O gas = Acid (liquid) + Hydrochloric or Hydrobromic acid (gas) :

	Chloride	Bromide
Acetic	17.5	13.8
Butyric (normal)	14.75	12.84
Butyric (iso-)	13.08	13.01
Valeric acid (iso-), from valerin	12.66	12.58
„ „ by oxidation	13.43	12.60

Trimethylacetic chloride gave for :



For the conversion of acetic anhydride into the acid, Berthelot finds (*Compt. rend.* lxxx. 599) :



and by subtracting from the difference of these two numbers, viz. 13.92, the heat of solution of acetic acid, there remains for the heat of conversion of C²H⁴O³ into C²H⁴O² :



This value is regarded by Berthelot as more exact than the number 12.0 formerly obtained by the very slow action of water on the anhydride.

Heat of Solution and of Chemical Action in the Wet Way.

Influence of Temperature on the Heat of Solution and the Heat of Chemical Action in general. The following general law of the equivalence between heat and chemical change, founded on the principle of the equivalence between heat and mechanical work—in this instance molecular work—and on the general law of the conservation of energy, was enunciated by Berthelot in 1865 (*Ann. Chim. Phys.* [4], vi. 329) : *When a system of bodies, simple or compound, existing under given conditions, undergoes physical or chemical alterations which bring it into a new state without the aid of external mechanical actions, the quantity of heat evolved or absorbed during these changes depends exclusively on the initial and final states of the system, and is the same whatever may be the nature and results of the intermediate states.*

Now suppose a system of still uncombined bodies to be raised, by assumption of a number of heat-units, U, without experiencing chemical change, from the temperature *t* to the higher temperature *τ* ; then suppose combination to take place, and let the quantity of heat thereby evolved be denoted by Q. Next let the resulting compound, without experiencing any chemical change, be cooled from *τ* to *t* by abstraction of

V units of heat. Lastly, let Q_t be the number of heat-units evolved when the same bodies unite chemically at the temperature t ; then it follows from the general principle just enunciated that:

$$Q_\tau - Q_t = U - V.$$

If the interval of temperature $\tau - t$ be so chosen that neither the uncombined bodies nor any of the products of the reaction suffer a change of aggregation, the preceding equation may be written in this form:

$$Q_\tau - Q_t = (\Sigma c - \Sigma c_1)(\tau - t),$$

where Σc denotes the sum of the specific heats of the atoms of the uncombined bodies, and Σc_1 that of the combined bodies.

In the gaseous state, the quantity of heat evolved in chemical reactions is but little affected by temperature, on account of the slight differences between the specific heats of the gases before and after the reaction. The liquid state is, on the whole, the least favourable to the comparison of the quantities of heat evolved or absorbed in reactions, on account of the rapid alteration of the specific heat of liquids with the temperature, whereas the alterations of the quantities of heat evolved, referred to the solid state, consequent on a change in the initial temperature, mostly fall within the limits of error of observation (Berthelot, *Compt. rend.* lxxviii. 1670).

Evolution of Heat in Solution at various Temperatures, and in the Dilution of Concentrated Solutions.—Let C be the molecular heat of the salt; nH_2O the quantity of water in which 1 mol. of the salt is dissolved; $18n + K$ the specific heat of this solution. Now from the observations of Schüller (1st Suppl. 668) it may be inferred that $K < C$ and even < 0 , for the more dilute solutions. Between the temperatures τ and t , the heat-capacity, U , of the constituents alone is equal to $(18n + C)(\tau - t)$, and that of the solution is $V = (18n + K)(\tau - t)$; consequently:

$$U - V = (C - K)(\tau - t),$$

and according to Berthelot's fundamental equation (*supra*):

$$Q_\tau - Q_t = (C - K)(\tau - t).$$

If now $K < C$, as it always is for solutions of an anhydrous salt in a large quantity of water, and if the solution at the temperature t is attended with absorption of heat, the quantity thus absorbed will be greater as the initial temperature τ is lower in comparison with t . On the other hand, the higher the initial temperature, the smaller will be the quantity of heat absorbed until, at a certain temperature, solution will take place without either evolution or absorption of heat. For initial temperatures higher than this, an evolution of heat takes place, increasing in amount as the initial temperature is higher. If, on the contrary, heat is evolved at a certain temperature t , the amount so evolved decreases as the initial temperature is lower, is reduced to nothing at a certain limit, and, on further lowering of the initial temperature, passes into a continually increasing absorption of heat.

For the temperature τ of solution, attended either by evolution or by absorption of heat, we have the equation:

$$Q_\tau = Q_t + U - V = Q_t + (18n + C)(\tau - t) - (18n + K)(\tau - t) = 0,$$

whence

$$\tau = -\frac{Q_t}{C - K} + t.$$

For example, Berthelot finds that the solution of anhydrous sodium sulphate in water at 21.5° is attended with the evolution of 780 units of heat.

Na_2SO_4 (142 grm.) + $400H_2O$ (7200 grm.) evolves 780 gram-degrees.

From this and the molecular heats of the salt and its solution, the temperature at which dissolution takes place without thermal change may be calculated as follows: For the solid salt, the molecular heat is 32.2, that of the initial system is therefore $7200 + 32.2 = 7232.5$. For the final system, that is to say, the resulting solution, we have:

	Specific heat	Molecular heat	$U - V$	τ
according to Schüller (1)	0.9835	7222	$(7232.5 - 7222)(\tau - 21.5)$	-52.8
„ Marignac (2)	0.9805	7199	$(7232.5 - 7199)(\tau - 21.5)$	-2.8
„ Thomsen (3)	0.976	7166	$(7232.5 - 7166)(\tau - 21.5)$	$+9.8$

(1) 1st. Suppl. 668.

(2) 2nd. Suppl. 601.

(3) *Ibid.* 599.

The preceding values of τ are calculated from the equation $Q_t = 780 + U - V$

whence, according to Schüller, $\tau = -\frac{780}{10.5} + 21.5 = -52.8^\circ$

$$\text{,, Marignac, } \tau = -\frac{780}{35.5} + 21.5 = -2.8^\circ$$

∴ Then, $\tau = -\frac{780}{66.5} + 21.5 = +9.8^\circ$

From direct observations at $+2.5^{\circ}$, $+3^{\circ}$, and $+3.9^{\circ}$, all of which indicated absorption of small quantities of heat, Berthelot infers that the temperature at which no thermal change would take place is about $+7^{\circ}$, which is intermediate between those deduced from the observations of Marignac and Thomsen. The accuracy of the calculation of τ is diminished by the fact that the divisor results from a small difference between two large experimental numbers, so that small errors in the determination of the latter will exert a considerable influence on the result of the calculation. Moreover, the calculation is based on the assumption that within the observed limits of temperature no change takes place in the heat-capacity either of the solution or of its constituents.

Crystallised potassium carbonate, $K^2CO^3.1\frac{1}{2}H^2O$, dissolves at ordinary temperatures with absorption of heat, and calculation shows that within the limits of temperature accessible to experiment, dissolution is attended sometimes with evolution, sometimes with absorption of heat. Berthelot observed the following thermal changes:

$$\text{K}^2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O} + 360\text{H}_2\text{O} \begin{cases} \text{at } 17.6^\circ & \cdot & \cdot & - 244 \text{ gram-degrees} \\ \text{about } 32^\circ & \cdot & \cdot & + 240 \quad \text{"} \end{cases}$$

The point of no thermal change must be situated near 25°. By similar calculations it is found that the absorption of heat which takes place on dissolution at ordinary temperatures becomes nothing and then passes into evolution of heat:

for KCl	in 100 H ² O	at about 130°	
„ NaNO ³	in 100 H ² O	„	160
„ KNO ³	in 200 H ² O	„	200

For the dilution of the solution of 1 mol. of a salt in n mol. water by addition of n_1 mol. water, $U = [18(n + n_1) + K](\tau - t)$ and $V = [18(n + n_1) + K_1](\tau - t)$: therefore

$$Q_r = Q_t + (K - K_1)(\tau - t).$$

Now as K is always greater than K_1 , the evolution of heat on dilution increases as the initial temperature is greater; consequently an absorption of heat taking place at t_0 gradually diminishes as the initial temperature increases, then becomes nothing, and passes into a continually increasing evolution of heat. For the temperature of dilution without thermal change, we have the equation

$$Q_r = Q_f + (K - K_f)(\tau - t) = 0;$$

whence

$$\tau = \frac{Q_t}{K - K_1} + t$$

(Berthelot, *Compt. rend.* lxxviii. 1722-1730).

By further experiments (*Ann. Chim. Phys.* [5], ix, 43) Berthelot finds that the heat of solution of slightly soluble bodies exhibits the same changes of sign and magnitude as those above noticed in very soluble bodies:

Calcium Hydrate, at about 15°	+	3
Strontium Sulphate, SrSO ₄ , anhydrous	{ at ordinary temperatures. a little below 15° above 25°	nearly 0
Calcium Sulphate, CaSO ₄ .2H ₂ O		positive
		negative
Lead Chloride		— 6
Potassium Picrate, C ⁶ H ³ (NO ₂) ³ K		— 10

Berthelot takes a similar view of the thermal changes which occur in crystallisation, precipitation, conglutination, and the conversion of an amorphous into a crystalline body, and proposes, as a differential method of measuring the specific heats of dilute solutions, the determination of the magnitude $U - V$ by two mixture experiments to be carried out at temperatures differing from one another by 10 or 15 degrees, the calculation being then performed according to the equation $U - V = (K - K_1)(\tau - t)$.

On the influence of temperature on the Heat of Chemical Combination in the Wet way, see also Thomson (*Deut. Chem. Ges. Ber.* vii. 1330-1345; *Jahresb. f. Chem.* 1873, 64).

Relations between the Heat of Solution of Salts and the Density of the Vapours evolved from their Solutions.—It has been shown by Kirchhoff (*Pogg. Ann.* cxciii. 196) that the thermic effect produced in the dissolution of a solid or liquid body in water is related to the vapour-density of the solution in the manner represented by the formula—

$$dQ_t = ATVF \frac{d}{dt} \log \left(\frac{F}{t} \right) dm, \quad \text{---}^{\text{---}}$$

in which dQ denotes the heat absorbed on addition of the weight dm of the substance at the temperature t ; $A = \frac{1}{425}$, the heat-equivalent of the unit of work; $T = t + 273$ the absolute temperature; F the maximum tension of water-vapour at the same temperature.

The correctness of this theory has been demonstrated by Montier (*Ann. Chim. Phys.* [4], xxviii. 515–529), by comparison with the experiments of Wüllner (iii. 95) on the vapour-tensions of various salt-solutions at different degrees of concentration, together with those of Person (*Jahresb. f. Chem.* 1851, 57) on the heat of solution of the same salts under similar conditions.

Constitution of Acids and Salts in Solution (Berthelot, *Compt. rend.* lxxxi. 844–849). The relative strength of acids and bases may be estimated by the extent to which their salts are decomposed by increasing quantities of water, as indicated by the accompanying evolution or absorption of heat.

Strong acids and bases, dissolved in separate portions of water and then united in equivalent quantities, form neutral stable salts, which disengage quantities of heat nearly constant for the different acids and bases of this category. This quantity of heat does not seem to vary on the addition of a fresh portion of water, or of a base or acid identical with or differing from those already in combination. From this it may be inferred that water does not tend to separate such bases and acids, at least in any appreciable manner. To such a class belong the chlorides, nitrates, and neutral sulphates of the fixed alkalis.

Weak acids, on the other hand, combining even with strong bases, form salts which are decomposed by water, the decomposition increasing with the amount of water added, and decreasing with the amount of base or acid. The progress of this decomposition is not always the same, but increases sometimes indefinitely, sometimes up to a certain limit, depending on the amount of water added. This is observed in borates, carbonates, alkaline phenates, and even in acetates, butyrates, valerates, &c.

Sometimes the decomposition of a neutral salt takes place almost entirely on the first addition of water, in such a manner that an absorption of heat occurs nearly equal to that disengaged in the initial formation of the alkaline salt; this is the case with the alkaline compounds derived from alcohol, mannite, glycerin, &c. In salts containing weak bases, such as the oxides of the heavy metals, the decomposing action of water shows itself distinctly even in presence of strong acids, and still more in presence of weak acids. The ammonia-salts of strong acids likewise show signs of decomposition by water, and in those of weak acids the decomposition is much more evident. Thus the neutral carbonate and phenate of ammonia are decomposed by water much more readily than the carbonates and phenates of the fixed alkalis; and between dissolved alkali carbonates and the nitrate, chloride, or sulphate of ammonium, double decomposition takes place, resulting in the formation of ammonium carbonate, and the union of the strongest acid with the strongest base, producing the most stable salt.

The following law, founded on thermo-chemical investigations, is laid down by Berthelot (*Bull. Soc. Chim.* [2], xix. 156). *The salt whose formation is attended with the greatest evolution of heat is always produced when the salts at whose expense its formation takes place are present in the solution in a state of partial decomposition. The sum of the reactions determined by the formation of this principal reaction is not however necessarily accompanied by the greatest possible evolution of heat, but may even be attended with absorption of heat.* Thus, for example, potassium carbonate in solution decomposes ammonium sulphate, and is converted entirely or nearly so into potassium sulphate with absorption of 3.2 units of heat. The point to be determined is therefore the stability of the salts in presence of water. This can in many cases be measured by the thermic changes accompanying dissolution and dilution, as in the case of ammonium salts with weak acids, which decompose to an extent increasing with the quantity of water present (*2nd Suppl.* 628, 629, 631).

The decomposition of ammonia-salts containing strong acids, the sulphate for example, which is slight and not sensible to the thermometer, may be recognised by the acid reaction produced, and by the alkalimetric analysis of the distillate.

If, for example, only a few ten-thousandths of the whole are decomposed, the addition of an alkaline carbonate disturbs the equilibrium so far as to produce complete conversion into potassium sulphate and ammonium carbonate, because free sulphuric acid cannot exist in its presence, the formation of potassium sulphate disengaging a greater quantity of heat than that of the carbonate. Ammonium carbonate is also completely decomposed by an equivalent quantity even of dilute sulphuric acid, as shown by the thermic changes which take place (Berthelot, *Jahresh. f. Chem.* 1872, 91). A similar explanation applies to the double decomposition of metallic salts. Thus, in consequence of the partial decomposition of dissolved ferric nitrate or sulphate, the addition of sodium acetate gives rise, according to thermal observations, to almost complete decomposition (*ibid.* 84; *2nd Suppl.* 287). Of all the salts whose formation is possible, the one actually produced is that whose formation is attended with the greatest evolution of heat. The same rule determines also the action of acids on dissolved salts (*Jahresh. f. Chem.* 1872, 90; *2nd Suppl.* 286). If the salt which evolves most heat is stable in presence of water, its formation will be complete; but if it suffers partial decomposition under the influence of water, its formation will be limited, in proportion to the degree of its stability. The above-mentioned rule, which is applicable to all saline solutions, is regarded by Berthelot as confirmatory of the general thermochemical principle, according to which every chemical change which takes place without external influence results in the formation of that body or these bodies whose production is attended with the greatest evolution of heat.

Redissolution of Precipitates by Acids.—Berthelot finds that the laws which regulate the division of a base between two acids and the formation of soluble salts within a solution (*2nd Suppl.* 286) are applicable also to insoluble salts, inasmuch as these latter are completely decomposed and dissolved by stronger acids, which act on the base of the salt with greater evolution of heat. Insoluble silver acetate for example is immediately converted by nitric acid into the soluble nitrate:

$\text{NO}^3\text{H dilute} + \text{C}^2\text{H}^3\text{AgO}^2 = \text{NO}^3\text{Ag dilute} + \text{C}^2\text{H}^4\text{O}^2 \text{ dissolved, gives } -3.5 \text{ kil.-deg.}$

But this absorption of heat is due to the conversion of a solid into a dissolved body: for calculation gives—

$\text{NO}^3\text{H dilute} + \text{C}^2\text{H}^3\text{AgNO}^2 = \text{NO}^3\text{Ag solid} + \text{C}^2\text{H}^4\text{O}^2 \text{ dissolved } + 2 \text{ kil.-deg.}$

and if the two acids were separated by water, the evolution of heat would amount even to 9 kil.-degs. A number of similar cases might be adduced in which a salt insoluble in water is completely dissolved by a monobasic acid. The dissolution of insoluble carbonates by monobasic acids, such as nitric or hydrochloric, in solutions concentrated but containing a quantity of water sufficient to dissolve the carbonic acid, is likewise complete. In dilute solutions the action is attended sometimes with evolution, sometimes with absorption of heat (silver carbonate and nitric acid). Thermic measurements also show that 1 mol. precipitated calcium tartrate, $\text{C}^4\text{H}^4\text{CaO}^6$, must be completely decomposed by 2 mols. hydrochloric acid. A similar reaction takes place between barium citrate and dilute hydrochloric acid, and between barium tartrate or citrate and dilute sulphuric acid (*Compt. rend.* lxxvii. 393).

Solution of Mixed Salts.—The thermic relations in the solution of mixed salts in water, and the accompanying double decompositions have been investigated by A. Winkelmann (*Pogg. Ann.* cxlix. 492-521). The general result may be stated in the following propositions: (1). In salts which do not suffer mutual decomposition when dissolved together, the law observed by Person (*Ann. Chim. Phys.* [3], xxxiii. 448) that the quantity of heat absorbed in the dissolution of a mixture of salts is equal to the sum of the quantities absorbed in the dissolution of the individual salts—is nearly true, and the more nearly as the solutions are less concentrated. The specific heat of the solution of such a saline mixture is also nearly equal to the mean specific heat of equally concentrated solutions of the individual salts, of which the mixed solution may be supposed to be ultimately constituted. (2). The form of the compounds in which acids and bases are introduced into the solution is not always a matter of indifference, inasmuch as the state of equilibrium which is ultimately established in the solution may depend upon that form. Instances of this are afforded by ammonium nitrate and sodium chloride on the one hand, and sodium nitrate and ammonium chloride on the other. The following comparison shows the deviation from Person's first law, which may take place in mixtures of salts which do not undergo mutual decomposition when dissolved in water. The mixture of these salts in equally concentrated solutions is usually attended with a rise of temperature, as observed by Marignac (*2nd Suppl.* 635); Winkelmann however, as also Marignac, has noticed some cases in which a fall of temperature is produced, thus—

Rise of temperature for—

KCl and NaCl.

KCl and KNO³.NaCl and NaNO³.KCl and NH⁴Cl.NH⁴Cl and NH⁴NO³.*Fall of temperature for—*NaCl and NH⁴Cl.NaNO³ and NH⁴NO³.

For the combinations in the first group, therefore, the quantity of heat calculated according to Person's first law, as required for the solution of a mixture of salts, is greater than the quantity actually used up, while for those in the second group it is less. But in both cases the differences between the observed and the calculated quantities are so small that for low degrees of concentration they fall altogether within the limits of observational error.

Heat of Combination and Specific Heat of Liquid Mixtures.—Winkelmänn (*Pogg. Ann.* cl. 592-619; cli. 512) has determined these data for mixtures of alcohol and benzin,* of alcohol and carbon disulphide, and of benzin and carbon disulphide, in the first case at three, in the other two at two different temperatures. The densities and the specific heats of the individual constituents were as follows:

Alcohol.

Sp. gr. at 16.03° = 0.7946.

Sp. heat K_t = 0.5721 + 0.001443*t* + 0.0000122*t*², between 3.82 and 28.18°.*Benzin.*

Sp. gr. at 16.50° = 0.6986.

Sp. heat K_t = 0.5244 + 0.000220*t*, between 3.32° and 19.06°.*Carbon Disulphide.*

Sp. gr. at 16.06° = 1.2665.

Sp. heat K_t = 0.2575 + 0.000182*t*, between 4.47° and 18.62°.

The mixing of alcohol and benzin, alcohol and CS², benzin and CS², is attended with a fall of temperature, and the amount of heat absorbed on mixing 1 gram. of either constituent with varying quantities of the other, increases with the quantity of the latter constituent. In this case, therefore, the same law holds good that is observed in the solution of salts at comparatively low temperatures, namely, that the quantity of heat absorbed in the act of solution increases with the quantity of water used. A comparison of the quantities of heat required for the formation of a given weight of a mixture from different proportions of its constituents, always exhibits a maximum for a mixture of equal parts of the two. From this point, in the three mixtures above mentioned, the quantities of heat consumed diminish most quickly on the side where the mixture contains a predominating quantity of that constituent which has the greater specific heat. The mixtures of alcohol and water form, in respect of their thermal relations, a peculiar group, in which, on the contrary, more heat is evolved on mixing 1 gram of alcohol with a larger quantity than with a smaller quantity of water.

The following table exhibits the specific heats and heats of mixing of mixtures of alcohol and water, as determined on the one hand by Winkelmänn, and on the other by Dupré a. Page (*Phil. Mag.* [4], xxxviii. 153; see also 2nd Suppl. 474). Series I. and III. show the quantities of heat evolved in the formation of 5 grams of the mixture referred to the initial temperature 17°; series II. and IV. the specific heats of the mixtures for the interval of temperature 17.4° to 20.5°.

Alcohol in 10 pts. of mixture	Dupré a. Page		Winkelmänn	
	I	II	III	IV
1	26.68	1.0358	25.90	1.0302
2	43.95	1.0436	42.70	1.0474
3	47.98	1.0260	47.23	1.0337
4	44.86	0.9680	42.60	0.9872
5	35.58	0.9063	35.02	0.9243
6	27.26	0.8433	26.72	0.8662
7	18.82	0.7844	19.05	0.8060
8	12.48	0.7169	12.06	0.7389
9	7.70	0.6576	6.54	0.6746

The somewhat considerable differences between these numbers follow a regular order in the specific heats, but in the heats of mixture they are quite irregular.

On the specific heats of mixtures of alcohol with water, carbon disulphide, chloro-

* 'Benzin,' also called 'ligroin,' is a constituent of petroleum; b. p. 60°-80°; not to be confounded with benzene.

form and benzin, see also Schüller (2nd Suppl. 477), where, however, benzin (from petroleum) is erroneously called 'benzene.'

Heat of Combination referred to the Solid State. Berthelot (*Compt. rend.* lxxvii. 24-32) considers that in estimating the quantities of heat evolved in the reaction between dissolved bases and acids, sufficient account has not been taken of the double decompositions occurring in solutions. Such decompositions indeed cannot be foreseen, except by calculation of the thermal action which would take place between the bodies if they were separated from the water, together with the investigation of the special action of the solvent upon each. He has, therefore, referred the quantities of heat evolved to the solid and crystalline state, the calculated values for which alter but little with the temperature, in consequence of the smallness of the alteration in the specific heat. For the calculations in question it is necessary to know, not only the quantities of heat evolved in the reactions between the dissolved bodies, but likewise the heat of solution of these bodies. With this view Berthelot has determined the heats of solution of the following compounds:

HEAT OF SOLUTION OF SALTS. 1 PT. SALT DISSOLVED IN 50-100 PTS. WATER.

1. *Monobasic Salts.*

Formates		Acetates		Benzoates, Picrates, &c.	
$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ cryst.	-2.35	$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ cryst.	-2.13	$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ about	-6.5
CH^{O}^2 liquid	0.08	$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ liquid about 23°	0.24	$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ (pivalate) solid	0.34
		$\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ " " 7°	0.40	$\text{C}^{\text{H}}\text{I}^{\text{O}}(\text{NO}^2)^2\text{O}$	-7.10
CHIKO^2 dry	-0.93	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{KO}^2$ dry	3.27	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{KO}^2$	-1.18
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{KO}^2$ fused	3.21	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NaO}^2$	0.78
CHINaO^2 dry	-0.52	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NaO}^2$ dry	4.08	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NH}^{\text{O}}^2$	-2.69
$\text{CHINH}^{\text{O}}^2$	-2.94	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NaO}^2$ fused	4.23		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NaO}^2 + 3\text{H}^{\text{O}}$ •	4.58	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NO}^2$ (pivalate) *	7.35 (?)
$\text{CHICa}^{\frac{1}{2}}\text{O}^2$	0.33	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Ca}^{\frac{1}{2}}\text{O}^2$	3.51		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Ca}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$ •	2.68	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{K}(\text{NO}^2)^2\text{O}$	-10.0
$\text{CHISr}^{\frac{1}{2}}\text{O}^2$	0.31	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Sr}^{\frac{1}{2}}\text{O}^2$	2.78	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Na}(\text{NO}^2)^2\text{O}$	-6.44
$\text{CHISr}^{\frac{1}{2}}\text{O}^2 + \text{H}^{\text{O}}$	-2.73	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Sr}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$	2.63	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{NH}^{\text{O}}(\text{NO}^2)^2\text{O}$	-8.7
$\text{CHBa}^{\frac{1}{2}}\text{O}^2$	-1.22	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Ba}^{\frac{1}{2}}\text{O}^2$	2.62		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Ba}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$	-0.41	MnO^2K	-10.30
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Mn}^{\frac{1}{2}}\text{O}^2$ •	6.12		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Mn}^{\frac{1}{2}}\text{O}^2 + 2\text{H}^{\text{O}}$	0.79	$\text{NO}^2\text{Ba}^{\frac{1}{2}}$	-2.48
$\text{CHZn}^{\frac{1}{2}}\text{O}^2$	1.99	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Zn}^{\frac{1}{2}}\text{O}^2$	4.91	$\text{NO}^2\text{Ba}^{\frac{1}{2}} + \frac{1}{2}\text{H}^{\text{O}}$	-4.30
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Zn}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$	3.18		
$\text{CHZn}^{\frac{1}{2}}\text{O}^2 + \text{H}^{\text{O}}$	-1.20	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Zn}^{\frac{1}{2}}\text{O}^2 + \text{H}^{\text{O}}$	2.12	CyKO	-5.17
$\text{CHICu}^{\frac{1}{2}}\text{O}^2$	0.26	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Cu}^{\frac{1}{2}}\text{O}^2$	1.21	CyKS about	-5.70
$\text{CHICu}^{\frac{1}{2}}\text{O}^2 + 2\text{H}^{\text{O}}$	-3.92	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Cu}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$	0.40		
$\text{CHPb}^{\frac{1}{2}}\text{O}^2$	-3.45	$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Pb}^{\frac{1}{2}}\text{O}^2$	0.70		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{Pb}^{\frac{1}{2}}\text{O}^2 + \frac{1}{2}\text{H}^{\text{O}}$	-2.77		
		$\text{C}^{\text{H}}\text{I}^{\text{O}}\text{AgO}^2$ •	-4.30		
Nitrates		Chlorides		Bromides, Iodides, Cyanides	
NO^2K	-8.29	KCl	-4.19	KBr	-5.45
NO^2Na	-4.66	NaCl	-1.08	NaBr	-0.29
NO^2NH^4	-6.20	NH^4Cl	-4.00	$\text{NaBr} + 2\text{H}^{\text{O}}$	-4.45
$\text{NO}^2\text{Ca}^{\frac{1}{2}}$	+1.6 (?)			KI	-5.32
$\text{NO}^2\text{Ca}^{\frac{1}{2}} + 2\text{H}^{\text{O}}$	-3.81			NaI	+1.30
$\text{NO}^2\text{Sr}^{\frac{1}{2}}$	-2.54	$\text{Sr}^{\frac{1}{2}}\text{Cl}$	5.48	$\text{NaI} + 2\text{H}^{\text{O}}$	-3.98
$\text{NO}^2\text{Sr}^{\frac{1}{2}} + \frac{1}{2}\text{H}^{\text{O}}$	-6.48	$\text{Sr}^{\frac{1}{2}}\text{Cl} + 3\text{H}^{\text{O}}$	-3.65	KCy	-2.86
$\text{NO}^2\text{Ba}^{\frac{1}{2}}$	-4.64	$\text{Ba}^{\frac{1}{2}}\text{Cl}$ •	0.82	$\text{Na}^{\frac{1}{2}}\text{Cy}$	-4.36
		$\text{Ba}^{\frac{1}{2}}\text{Cl} + \text{H}^{\text{O}}$	-2.61	$\text{Hg}^{\frac{1}{2}}\text{Cy}$	-1.60
$\text{NO}^2\text{Pb}^{\frac{1}{2}}$	-4.11	$\text{Pb}^{\frac{1}{2}}\text{Cl}$ •	-2.0		
NO^2Ag	-5.73	$\text{Hg}^{\frac{1}{2}}\text{Cl}$	-1.52	$\text{NH}^4\text{H}^{\text{O}}\text{S}$	-3.25
		$\text{Sn}^{\frac{1}{2}}\text{Cl} + \text{H}^{\text{O}}$	-2.68		

* $\text{C}^{\text{H}}\text{I}^{\text{O}}^2$ (pivalate, 1 eq. in 6 litres) + $\text{KO}^{\frac{1}{2}}$ (1 eq. in 2 l.) 13.59. This number, which is very near to that for acetic acid, is not altered by an excess either of acid or of alkali.

2. Basic Salts.

Sulphates		Oxalates		Tartrates	
SO^3	37.30	$\text{C}^2\text{H}^2\text{O}^4$	- 3.29	$\text{C}^4\text{H}^4\text{O}^6$	- 3.45
SH^2O^4 cryst.	16.06	$(\text{C}^2\text{H}^2\text{O}^4 + 2\text{H}^2\text{O})$	- 8.49		
SH^2O^4 liquid	16.92	$\text{C}^2\text{K}^2\text{O}^4$	- 4.74	$\text{C}^4\text{H}^4\text{K}^2\text{O}^6$	- 3.56
SO^3K^2	- 6.04	$\text{C}^2\text{K}^2\text{O}^4 + \text{H}^2\text{O}$	- 7.73	$\text{C}^4\text{H}^4\text{K}^2\text{O}^6 + \text{H}^2\text{O}$	- 5.56
SO^3KH	- 3.23	$\text{C}^2\text{Na}^2\text{O}^4$	- 4.30	$\text{C}^4\text{H}^4\text{Na}^2\text{O}^6$	- 1.12
SO^3Na^2	- 0.76*	C^2HNaO^4	- 5.60	$\text{C}^4\text{H}^4\text{Na}^2\text{O}^6 + 2\text{H}^2\text{O}$	- 5.88
$\text{SO}^3\text{Na}^2 + 10\text{H}^2\text{O}$	- 18.10	$\text{C}^2\text{HNaO}^4 + \text{H}^2\text{O}$	- 9.50	$\text{C}^4\text{H}^4\text{NaO}^6$	- 5.66
SO^3NaH	- 0.76	$\text{C}^2(\text{NH}^2)\text{O}^4$	- 7.98	$\text{C}^4\text{H}^4\text{NaO}^6 + \text{H}^2\text{O}$	- 8.54
$\text{SO}^3(\text{NH}^2)^2$	- 2.70	$\text{C}^2(\text{NH}^2)\text{O}^4 + \text{H}^2\text{O}$	- 11.47	$\text{C}^4\text{H}^4\text{NaKO}^6$	- 1.87
				$\text{C}^4\text{H}^4\text{NaKO}^6 + 4\text{H}^2\text{O}$	- 12.34
		Carbonates			
CO^3K^2	6.54	CO^3KH	- 5.32		
$\text{CO}^3\text{K}^2 + \frac{3}{2}\text{H}^2\text{O}$	- 0.24	CO^3NaH	- 4.27		
CO^3Na^2	5.54	$\text{CO}^3\text{NH}^2\text{H}$	- 6.28		

* This number 0.76 agrees very well with those found by Graham, 0.76, and by Favre 0.75, but differs greatly from that of Thomsen, (p. 288) viz. 0.06, which is probably due to an error of observation.

Formation of Crystallised Hydrates.—The heats of formation of these hydrates, given in the following table, are easily computed from the numbers above tabulated. The numbers for the hydrates of acids and bases exhibit no simple relation to each other, but they are much larger than those for the hydrates of salts containing water of crystallisation, which likewise do not bear any simple relation to one another. Sodium acetate, for example, loses the whole of its water of crystallisation in a vacuum, whilst the combination of each molecule of water is attended with the evolution of 1.46 heat-units; cupric acetate, on the other hand, which gives off nine times less heat, viz. 0.16 heat-units, does not part with its water in a vacuum.

SO^3 solid	+	H^2O solid	=	SO^3H^2 solid	.	.	.	19.8 kil.-degrees.
BaO	"	+	"	=	BaH^2O^2	"	.	16.2 "
SrO	"	+	"	=	SrH^2O^2	"	.	15.8 "
CaO	"	+	"	=	CaH^2O^2	"	.	13.6 "

$\text{C}^2\text{H}^2\text{O}^4$	+	$2\text{H}^2\text{O}$ solid	3.34 or for H^2O	1.66 kil.-degrees.
KHO	+	$2\text{H}^2\text{O}$	9.63	4.82 "
BaH^2O^2	+	$9\text{H}^2\text{O}$	11.44	1.28 "
SrH^2O^2	+	$9\text{H}^2\text{O}$	11.84	1.32 "
BaCl^2	+	$2\text{H}^2\text{O}$	4.00	2.00 "
SrCl^2	+	$6\text{H}^2\text{O}$	9.68	1.62 "
NaBr	+	$2\text{H}^2\text{O}$	1.30	0.64 "
NaI	+	$2\text{H}^2\text{O}$	2.42	1.22 "
SO^3Na^2	+	$10\text{H}^2\text{O}$	4.56	0.46 "
$\text{C}^2\text{H}^2\text{NaO}^2$	+	$3\text{H}^2\text{O}$	4.37	1.46 "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Ca}$	+	H^2O	1.66	0.24 "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Sr}$	+	$\frac{1}{2}\text{H}^2\text{O}$	- 0.42	— "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Ba}$	+	$3\text{H}^2\text{O}$	1.76	0.58 "
$(\text{CHO}^2)^2\text{Sr}$	+	$2\text{H}^2\text{O}$	3.20	1.60 "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Zn}$	+	$2\text{H}^2\text{O}$	4.00	2.36 "
"	+	H^2O	2.02	2.02 "
$(\text{CHO}^2)^2\text{Zn}$	+	$2\text{H}^2\text{O}$	3.52	1.76 "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Cu}$	+	H^2O	0.16	0.16 "
$(\text{CHO}^2)^2\text{Cu}$	+	$4\text{H}^2\text{O}$	2.64	0.66 "
$(\text{C}^2\text{H}^2\text{O}^2)^2\text{Pb}$	+	$3\text{H}^2\text{O}$	2.64	0.88 "

Formation of Acid Salts, Double Salts, &c.

SO^3K^2	+	SO^3	=	$\text{S}^2\text{O}^7\text{K}^2$.	.	26.0 kil.-degrees.
$\text{S}^2\text{O}^7\text{K}^2$	+	H^2O solid	=	$2\text{SO}^3\text{KH}$.	.	8.6 "
SO^3K^2	+	SO^3H^2 solid	=	$2\text{SO}^3\text{KH}$.	.	15.2 "
SO^3Na^2	+	SO^3H^2 solid	=	$2\text{SO}^3\text{NaH}$.	.	16.0 "
$\text{C}^2\text{Na}^2\text{O}^4$	+	$\text{C}^2\text{H}^2\text{O}^4$	=	$2\text{C}^2\text{HNaO}^4$.	.	3.8 "
$\text{C}^4\text{H}^4\text{Na}^2\text{O}^6$	+	$\text{C}^4\text{H}^4\text{O}^6$	=	$2\text{C}^4\text{H}^2\text{NaO}^6$.	.	6.6 "
$\text{C}^4\text{H}^4\text{K}^2\text{O}^6$	+	$\text{C}^4\text{H}^4\text{Na}^2\text{O}^6$	=	$2\text{C}^4\text{H}^2\text{NaKO}^6$.	.	0.0 "

Formation of Salts from Acids and Bases.

Anhydrides and Bases	$\text{SO}^3 + \text{BaO} = \text{SO}^3\text{Ba}$	102.0 kil. degrees.
	$\text{SO}^3 + \text{SrO} = \text{SO}^3\text{Sr}$	95.6 "
	$\text{SO}^3 + \text{CaO} = \text{SO}^3\text{Ca}$	about 84.0 "
	$\text{SO}^3 + \text{PbO} = \text{SO}^3\text{Pb}$	60.8 "
	$\text{SO}^3 + \text{ZnO} = \text{SO}^3\text{Zn}$	45.0 "
Acids and Bases	$\text{SO}^3 + \text{CuO} = \text{SO}^3\text{Cu}$	42.6 "
	$\text{SO}^3\text{H}^2 + 2\text{KHO} = \text{SO}^3\text{K}^2 + 2\text{H}^2\text{O}$	solid 81.2 "
	$\text{SO}^3\text{H}^2 + 2\text{NaHO} = \text{SO}^3\text{Na}^2 + 2\text{H}^2\text{O}$	69.4 "
	$\text{SO}^3\text{H}^2 + \text{BaHO}^2 = \text{SO}^3\text{Ba} + 2\text{H}^2\text{O}$	65.4 "
	$\text{SO}^3\text{H}^2 + \text{SrHO}^2 = \text{SO}^3\text{Sr} + 2\text{H}^2\text{O}$	59.6 "
	$\text{SO}^3\text{H}^2 + \text{CaHO}^2 = \text{SO}^3\text{Ca} + 2\text{H}^2\text{O}$	50.8 "
	$\text{SO}^3\text{H}^2 + \text{PbHO}^2 = \text{SO}^3\text{Pb} + 2\text{H}^2\text{O}$	39.8 "
	$\text{SO}^3\text{H}^2 + \text{ZnHO}^2 = \text{SO}^3\text{Zn} + 2\text{H}^2\text{O}$	26.2 "
	$\text{SO}^3\text{H}^2 + \text{CuHO}^2 = \text{SO}^3\text{Cu} + 2\text{H}^2\text{O}$	21.0 "
	$\text{SO}^3\text{H}^2 + \text{KHO} = \text{SO}^3\text{KH} + \text{H}^2\text{O}$	48.2 "
Acid Salts	$\text{SO}^3\text{H}^2 + \text{NaHO} = \text{SO}^3\text{NaH} + \text{H}^2\text{O}$	42.7 "

The quantities of heat evolved increase with the stability of the products, but no simple relation or common constant can be traced between them.

Monobasic Salts.—The following numbers correspond with the reaction: Acid + Basic Hydroxide = Salt + Water. All the bodies regarded as solid:

CHKO^2	25.6	$\text{C}^3\text{H}^3\text{KO}^2$	21.8	$\text{C}^3\text{H}^3\text{KO}^2$ (pivalato)	19.8
CHNaO^2	22.5	$\text{C}^3\text{H}^3\text{NaO}^2$	18.4	$\text{C}^3\text{H}^3\text{KO}^2$	22.5
$\text{CHCa}^{\frac{1}{2}}\text{O}^2$	13.3	$\text{C}^3\text{H}^3\text{Ca}^{\frac{1}{2}}\text{O}^2$	10.6	$\text{C}^3\text{H}^3\text{NaO}^2$	17.4
$\text{CHSr}^{\frac{1}{2}}\text{O}^2$	16.7	$\text{C}^3\text{H}^3\text{Sr}^{\frac{1}{2}}\text{O}^2$	14.7	$\text{C}^3\text{H}^3\text{Ca}^{\frac{1}{2}}\text{O}^2$	7.7
$\text{CHBa}^{\frac{1}{2}}\text{O}^2$	18.6	$\text{C}^3\text{H}^3\text{Ba}^{\frac{1}{2}}\text{O}^2$	15.2		
$\text{CHZn}^{\frac{1}{2}}\text{O}^2$	6.1	$\text{C}^3\text{H}^3\text{Zn}^{\frac{1}{2}}\text{O}^2$	3.7		
$\text{CHCa}^{\frac{1}{2}}\text{O}^2$	5.2	$\text{C}^3\text{H}^3\text{Ca}^{\frac{1}{2}}\text{O}^2$	4.5		
$\text{CHPb}^{\frac{1}{2}}\text{O}^2$	10.2	$\text{C}^3\text{H}^3\text{Pb}^{\frac{1}{2}}\text{O}^2$	6.3		

Salts of Bibasic Acids.

Oxalates		Tartrates	
$\text{C}^2\text{K}^2\text{O}^4$	58.8 : 2 = 29.4	$\text{C}^2\text{H}^2\text{K}^2\text{O}^4$	53.8 : 2 = 26.9
$\text{C}^2\text{Na}^2\text{O}^4$	53.0 : 2 = 26.5	$\text{C}^2\text{H}^2\text{Na}^2\text{O}^4$	45.9 : 2 = 22.9
C^2NaHO^4	28.4	$\text{C}^2\text{H}^2\text{NaO}^4$	26.2
		$\text{C}^2\text{H}^2\text{NaKO}^4$	49.5

The heats of formation of bibasic salts exceed those of equivalent quantities of the corresponding monobasic salts, and those of the sulphates exceed those of the organic salts. The differences between the heats of the salts of the alkalis and alkaline earths are all of the same order of magnitude. All such regularities, however, are true only for the anhydrous salts. Solubility or insolubility has but little influence on the result, as may be seen by comparison of the sulphates with the formates or acetates.

Relations between the Heats of Solution in the preceding Table.—The potassium and sodium salts of the same acid often exhibit nearly constant differences: -3.1 for the chlorides; -3.7 for the nitrates; -3.6 for the picrates; -3.4×2 for the sulphates. Between the sodium and ammonium salts, the differences are: 2.9 for the chlorides, 2.5 for the nitrates, 1.7×2 for the sulphates, 2.3 for the picrates. Between the formates of potassium and sodium, the difference is only -0.4 ; between the acetates -0.8 ; between the oxalates -0.2×2 , &c. On the other hand, the anhydrous acetates of potassium, sodium, calcium, barium, and lead all exceed the corresponding formates by about 4.

Development of Heat and Changes of Volume attending the Solution of Anhydrous Salts (Favre & Valson, *Compt. rend.* lxxvii. 802-809). In the following table, which is a sequel to those already given (*2nd Suppl.* 292-303), P denotes the weight in grams of the equivalent of the salt; D the density of the solid anhydrous salt; $V = \frac{P}{D}$ the volume of 1 eq.; d the density of the normal solution, containing 1 eq.

of the salt in a litre; v the increase of volume, calculated therefrom, of 1 litre of water by dissolution of 1 eq. of the salt; $C = (V - v) \times 75.76$ kilogram-degrees of heat (see *2nd Suppl.* 302); C' the heat evolved in the dissolution of the salt, as determined by the mercury-calorimeter; $C - C'$ denotes, therefore, the amount of internal work expressed in kil.-degrees of heat:

Change of Volume and Development of Heat in the Solution of Anhydrous Salts.

Salt	P	D	$V = \frac{V}{D}$ c.c.	d	v	$V - v$ c.c.	$\frac{V - v}{v}$	C kil.-degrees	$\frac{C}{v}$ kil.-degrees	C - C' kil.-degrees
$\frac{1}{2}\text{B}^+\text{O}^-\text{Na}^+$	101	2.371	42.6	1.0920	8.2	34.4	0.87	260.614	5.092	255.522
$\frac{1}{2}\text{B}^+\text{O}^-(\text{NH})^+$	96	—	—	1.0678	10.2	—	—	—	—	—
$\frac{1}{2}\text{CO}^+\text{Na}^+$	53	2.407	22.0	1.0519	1.0	21.0	0.95	227.280	3.658	223.622
$\frac{1}{2}\text{CO}^+(\text{NH})^+$	48	—	—	1.0178	10.3	—	—	—	—	—
$\frac{1}{2}\text{SO}^+\text{Al}^+$	57.17	2.672	21.4	1.0568	0.4	11.0	0.98	159.098	—	—
$\frac{1}{2}\text{SO}^+\text{Cu}^+$	80	3.707	21.6	1.0776	2.3	19.3	0.89	146.217	8.198	138.019
$\frac{1}{2}\text{SO}^+\text{Ca}^+$	65.83	2.743	24.0	1.0600	5.5	18.5	0.77	140.156	—	—
$\frac{1}{2}\text{SO}^+\text{Na}^+$	71	2.681	26.5	1.0606	9.8	16.7	0.70	126.519	0.354	126.165
$\frac{1}{2}\text{SO}^+\text{K}^+$	87	2.653	32.8	1.0662	19.6	13.2	0.40	100.003	-3.361	103.364
$\frac{1}{2}\text{SO}^+(\text{NH})^+$	66	1.766	37.4	1.0378	27.3	10.1	0.27	76.518	-0.979	77.497
NaF	42	2.793	15.0	1.0365	5.3	9.7	0.64	73.487	-0.205	73.692
KF	58	2.465	23.5	1.0468	10.7	12.8	0.55	96.273	3.135	99.408
NH_4F	37	1.972	18.8	1.0314	15.3	3.5	0.19	26.516	-1.417	27.933
$\frac{1}{2}\text{Cl}^+\text{Sr}^+$	79.5	3.035	26.1	1.0667	11.8	14.3	0.54	108.337	5.483	102.854
$\frac{1}{2}\text{Cl}^+\text{Ba}^+$	104.5	3.844	27.1	1.0887	44.8	12.3	0.45	93.185	1.172	92.013
$\frac{1}{2}\text{Cl}^+\text{Ca}^+$	55.5	2.160	25.7	1.0139	11.2	14.5	0.56	109.852	9.053	100.799
ClNa	58.5	2.143	27.3	1.0396	18.3	9.0	0.33	68.184	-1.002	69.186
ClK	74.5	1.976	37.7	1.0444	28.9	8.8	0.23	66.669	-4.402	71.131
ClNH_4	53.5	1.525	35.1	1.0157	37.2	-2.1	-0.06	15.910	-4.063	-11.874
$\frac{1}{2}\text{N}^+\text{O}^-\text{Sr}^+$	105.75	2.980	35.5	1.0811	22.8	12.7	0.36	96.215	-2.348	98.563
$\frac{1}{2}\text{N}^+\text{O}^-\text{Ba}^+$	131.5	3.208	40.8	1.1038	24.6	16.2	0.40	122.173	-4.583	127.314
$\frac{1}{2}\text{N}^+\text{O}^-\text{Ca}^+$	82	2.504	32.7	1.0578	23.0	9.7	0.29	73.487	+2.014	71.473
NO^+Na^+	85	2.241	37.9	1.0540	29.4	8.5	0.22	64.396	-4.842	69.238
NO^+K^+	101	2.093	48.3	1.0591	38.7	9.6	0.20	72.730	-8.330	81.060
NO^+NH_4	80	1.668	48.0	1.0307	47.9	0.1	0.02	0.758	-6.325	7.083
$\frac{1}{2}\text{Br}^+\text{Sr}^+$	123.75	3.985	31.1	1.1021	19.3	11.8	0.37	89.397	7.850	81.547
$\frac{1}{2}\text{Br}^+\text{Ba}^+$	149	4.645	32.1	1.1253	21.1	11.0	0.34	83.336	2.370	80.966
BrNa	103	3.198	32.2	1.0770	24.2	8.0	0.24	60.698	0.109	60.499
BrK	119	2.524	47.2	1.0800	36.1	11.4	0.23	84.094	-4.952	89.086
BrNH_4	98	2.429	40.3	1.0320	43.9	-3.6	-0.09	-27.274	-4.472	-22.802
INa	150	3.654	41.0	1.1105	35.6	5.4	0.13	40.910	1.762	39.148
IK	166	2.946	56.4	1.1135	47.2	9.2	0.16	69.699	-5.169	74.868
INH_4	145	2.480	50.8	1.1847	55.9	-5.1	-0.10	-38.638	-3.788	-35.050

Thermo-neutrality and Neutrality of Density. The term *thermo-neutrality* is employed by Favre & Valson (*Compt. rend.* lxxvii. 907) to express the fact that the quantity of heat evolved or absorbed when a salt is dissolved in water already containing equivalent quantities of other salts, is, for the most part, the same as it would be if the former salt were dissolved in pure water. When, for example, 1 eq. of sodium nitrate is dissolved in water containing 1 eq. potassium chloride and 1 eq. ammonium sulphate, an absorption of heat occurs, amounting to 4.702 kilogram-degrees; and the quantity absorbed on dissolving the same quantity of sodium-nitrate in pure water is 4.842, differing from the former by only 0.140; the amount of heat-absorption in the two cases may therefore be regarded as the same: in other words, the condition of thermo-neutrality is satisfied.

Neutrality of density has a similar meaning with regard to the density of the resulting solution, which is, in fact, an arithmetical mean between the densities of the solutions formed by dissolving each salt separately in the same quantity of water. This may be illustrated by the following example, in which the letters P, D, &c. have the same signification as in the table on p. 984.

	P	D	V	d	v	V - v	$\frac{V - v}{V}$
NO ³ Na	85	2.241	c.c. 37.9	1.0540	c.c. 29.4	c.c. 8.5	0.22
ClK	74.5	1.976	37.8	1.0444	29.0	8.8	0.23
SO ⁴ (NH ⁴) ₂ 2	66	1.766	37.4	1.0378	27.3	10.1	0.27
Mean	75.2	1.994	37.7	1.0454	28.6	9.1	0.24
Mixture	75.2	1.994	37.7	1.0445	29.4	8.3	0.22

In like manner the dissolution of 1 eq. cupric sulphate in pure water gives rise to the same thermic change as in water already containing 1 eq. potassium sulphate. Moreover, the precipitation of potassio-cupric sulphate by barium chloride produces the same evolution of heat as the precipitation of the two constituent salts. Hence it would appear that double salts, like potassio-cupric sulphate, cannot exist in solution, but are split up in the act of dissolving into their constituent salts, and then conform to the law of thermo-neutrality (*compare 2nd Suppl.* 293). Potassium sulphate and copper sulphate, dissolved together in equivalent proportions, also yield a solution in which the law of density-neutrality is satisfied, as shown by the following numbers:

	P	D	V	d	v	V - v	$\frac{V - v}{V}$
SO ⁴ K ₂ 2	87	2.653	c.c. 32.8	1.0662	c.c. 19.6	c.c. 13.2	0.40
SO ⁴ Cu 2	80	2.707	21.5	1.0777	2.1	19.4	0.90
Mean	83.5	3.180	27.1	1.0720	10.8	16.3	0.60
Mixtures	83.5	3.180	27.1	1.0717	21.1	16.0	0.59

Potassio-cupric sulphate and other neutral double salts appear, therefore, to yield solutions in which each of the constituent salts is in the same state as if it existed alone in the liquid. With *acid salts*, however, which in the crystallised state are true double salts, the case is different. Hydropotassic sulphate and its constituent salts, for example, when precipitated by barium chloride, yield the following quantities of heat:

		Kilogram-degrees
Dissolved alone, $\frac{\text{SO}^4\text{K}^2}{2}$, gives		2.879
“ $\frac{\text{SO}^4\text{Cu}}{2}$ ”		4.766
	Sum .	7.645
Dissolved acid salt, SO ⁴ KH, gives		8.450
	Difference .	0.805

The density-relations are shown in the following table :

	P	D	V	d	r	V - v	$\frac{V-r}{V}$
$\frac{\text{SO}^4\text{K}^2}{2}$	87	2.653	32.8	1.0662	19.6	13.2	0.40
$\frac{\text{SO}^4\text{Cu}}{2}$	49	1.818	26.5	1.0300	18.5	8.0	0.30
Mean	68	2.250	29.7	1.0481	19.0	10.6	0.35
Mixture	68	2.250	29.7	1.0155	21.5	8.2	0.27

Those salts which do not satisfy the law of thermo-neutrality when their dilute solutions are mixed together, are likewise found not to exhibit neutrality of density, thus :

				Kil.-degrees
$\frac{\text{Na}^2\text{O}}{2}$ dilute	+	$\frac{\text{CO}^2}{2}$ gas	= $\frac{\text{Na}^2\text{CO}^3}{2}$ dilute	12.940
NH^3 dissolved	+	$\frac{\text{SO}^4\text{H}^2}{2}$ dissolved	= $\frac{(\text{NH}^4)^2\text{SO}^4}{2}$ dilute	14.888
Sum				27.828
NH^3 dilute	+	$\frac{\text{CO}^2}{2}$ gas	= $\frac{(\text{NH}^4)^2\text{CO}^3}{2}$ dilute	8.473
$\frac{\text{Na}^2\text{O}}{2}$ dissolved	+	$\frac{\text{SO}^4\text{H}^2}{2}$ dissolved	= $\frac{\text{Na}^2\text{SO}^4}{2}$ dilute	16.301
Sum				24.774
Difference of the two sums				3.054
Heat of solution of $\frac{\text{Na}^2\text{CO}^3}{2}$ in pure water				-7.840
" " in water + $\frac{(\text{NH}^4)^2\text{SO}^4}{2}$				-10.700
Difference				2.860

The two differences agree nearly with one another, and there is no thermo-neutrality. With regard to the relations of density of these salts, the following results have been obtained :

	P	D	V	d	v	V - v	$\frac{V-v}{V}$
$\frac{\text{CO}^2\text{Na}^2}{2}$	53	2.420	21.9	1.0519	1.0	20.9	0.96
$\frac{\text{SO}^4(\text{NH}^4)^2}{2}$	66	1.776	37.4	1.0378	27.3	10.1	0.27
Mean	59.5	2.093	29.6	1.0448	14.1	15.5	0.61
Mixture	59.5	2.093	29.6	1.0391	19.7	9.9	0.33
$\frac{(\text{NH}^4)^2\text{CO}^3}{2}$	48	—	—	1.0178	29.7	—	—
$\frac{\text{Na}^2\text{SO}^4}{2}$	71	2.681	26.5	1.0606	9.8	16.7	0.63
Mean	59.5	—	—	1.03992	19.7	16.7	—

The values of d , v , &c. for the mixture differ considerably from the first means, but agree nearly with the second, showing that the salts Na^2CO^3 and $(\text{NH}^4)^2\text{SO}^4$ have been converted in the mixture into Na^2SO^4 and $(\text{NH}^4)^2\text{CO}^3$. Similar results have been obtained by Favre & Valson with sodium borate and ammonium sulphate. (See also Berthelot, *Compt. rend.* lxxvii. 971; *Jahresb. f. Chem.* 1873, 104.) Favre

a. Valson point out the agreement of their results with those of Berthelot on the constitution of salts in solution (*Compt. rend.* lxxiv. 48, 119; lxxv. 207, 263; *Ann. Chim. Phys.* [4], xxvi. 433; 2nd Suppl. 285), and to those of Thomson on the action of dilute sulphuric acid on solution of potassium sulphate (*Pogg. Ann.* cxxxviii. 497; *Jahresb.* 1860, 115).

Heat of Solution of Various Classes of Compounds.

Thomson (*Deut. Chem. Ges. Ber.* vi. 710-717) has collected together in the following table the results of his experiments on the heat evolved or absorbed in the dissolution of various salts and other bodies in water. The values are calculated for the molecule, i.e. for the weight represented by the formula. The quantity of water used to dissolve each substance is stated according to the number of water-molecules contained in the solution for each molecule of the substance dissolved.

Substance	Formula	Quantity of water in mols.	Thermic effect per mol. of substance
<i>1. Crystallised Chlorides, Bromides, and Iodides</i>			
Sodium Chloride	NaCl	200	- 1.18
Potassium „	KCl	200	- 4.44
Ammonium „	AmCl	100	- 4.41
Barium „	BaCl ² + 2H ² O	200	- 3.88
Strontium „	SrCl ² + 6H ² O	400	- 4.93
Calcium „	CaCl ² + 6H ² O	400	- 7.5
Magnesium „	MgCl ² + 6H ² O	400	- 4.34
Sodium Bromide	NaBr	400	+ 2.9
Potassium „	KBr	200	- 1.15
Ammonium „	NH ⁴ Br	200	- 5.08
Barium „	BaBr ² + 2H ² O	200	- 4.38
Strontium „	SrBr ² + 6H ² O	400	- 4.13
Calcium „	CaBr ² + 6H ² O	400	- 7.2
Sodium Iodide	NaI	450	- 4.93
Potassium „	KI	200	+ 1.22
Ammonium Iodide	AmI	200	+ 5.11
Gold Chloride, cryst.	Au ² Cl ⁶ H ² Cl ² + 7.3H ² O	200	- 3.55
Potassium Stannochloride	K ² Cl ² -SnCl ⁴	900	- 11.70
		800	- 3.38
<i>2. Liquid Chlorides and Bromine.</i>			
Stannic Chloride	SnCl ⁴	300	+ 29.92
Titanium „	TiCl ⁴	1600	+ 57.87
Silicon „	SiCl ⁴	3000	+ 69.26
Phosphorous Chloride	PCl ³	1000	+ 65.14
Bromine	Br ²	600	+ 1.08
<i>3. Nitrates.</i>			
Sodium Nitrate	NaNO ³	200	- 5.06
Potassium „	KNO ³	200	- 8.52
Ammonium „	NH ⁴ NO ³	200	- 6.32
Silver „	AgNO ³	100	- 6.16
Barium „	BaNO ³	200	- 5.44
Strontium „	SrN ² O ⁶	400	- 9.40
Calcium „	CaN ² O ⁶ .4H ² O	400	- 4.62
Magnesium „	MgN ² O ⁶ .6H ² O	400	- 7.2
Lead „	PbN ² O ⁶	400	- 4.22
		400	- 7.60
<i>4. Sulphates.</i>			
Sodium Sulphate	Na ² SO ⁴ + 10H ² O	600	- 18.81
		400	- 18.76
		200	- 18.55
		100	- 18.13
		50	- 17.46

Substance	Formula	Quantity of water in mols.	Thermic effect per mol. of substance
<i>Sulphates.</i> —Continued.			
Sodium Sulphate	Na_2SO_4	400	— 0.06
Potassium "	K_2SO_4	400	— 6.38
Ammonium "	$(\text{NH}_4)_2\text{SO}_4$	400	— 2.33
Thallous "	Tl_2SO_4	200	— 2.33
Barium "	BaSO_4	900	— 8.60
Strontium "	SrSO_4	—	— 5.58
Calcium "	$\text{CaSO}_4 + 2\text{H}_2\text{O}$	—	0
Magnesium "	$\text{MgSO}_4 + 7\text{H}_2\text{O}$	400	— 0.60
Zinc "	$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	400	— 3.91
Ferrous "	$\text{FeSO}_4 + 7\text{H}_2\text{O}$	400	— 4.24
Manganous "	$\text{MnSO}_4 + 5\text{H}_2\text{O}$	400	— 4.51
	$\text{MnSO}_4 + 4\text{H}_2\text{O}$	400	+ 0.04
Copper "	$\text{CuSO}_4 + 5\text{H}_2\text{O}$	400	+ 1.77
	$\text{CuSO}_4 + \text{H}_2\text{O}$	400	— 2.75
Nickel "	$\text{NiSO}_4 + 7\text{H}_2\text{O}$	400	+ 8.72
Cobalt "	$\text{CoSO}_4 + 7\text{H}_2\text{O}$	800	— 4.25
Cadmium "	$\text{CdSO}_4 + \frac{2}{3}\text{H}_2\text{O}$	800	— 3.57
Yttrium "	$\text{YSO}_4 + \frac{2}{3}\text{H}_2\text{O}$	400	+ 2.54
Lanthanum "	$\text{LaSO}_4 + 3\text{H}_2\text{O}$	400	+ 3.56
Beryllium "	$\text{BeSO}_4 + 4\text{H}_2\text{O}$	400	+ 1.50
Alumino-potassic Sulphate	$\text{K}_2\text{SO}_4 + \text{Al}_2\text{S}_2\text{O}_{12} + 24\text{H}_2\text{O}$	2400	+ 1.10
Chromo-potassic "	$\text{K}_2\text{SO}_4 + \text{Cr}_2\text{S}_2\text{O}_{12} + 24\text{H}_2\text{O}$	2400	— 20.24
		1600	— 22.30

5. *Acetates.*

Sodium Acetate	$\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$	400	— 4.81
Barium "	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$	800	— 1.07
Lead "	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$	800	— 6.14
Copper "	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$	400	+ 0.16
Erbium "	$\text{Er}(\text{C}_2\text{H}_3\text{O}_2)_2 + \frac{2}{3}\text{H}_2\text{O}$	1000	+ 0.45

6. *Potassium Salts.*

Potassium Chloride	KCl	200	— 4.44
" Bromide	KBr	200	— 5.08
" Iodide	KI	200	— 5.11
" Chlorate	KClO_3	400	— 10.04
" Nitrate	KNO_3	200	— 8.52
" Dithionate	$\text{K}_2\text{S}_2\text{O}_6$	500	— 12.99
" Sulphate	K_2SO_4	400	— 6.38
" Chromate	$\text{K}_2\text{Cr}_2\text{O}_7$	800	— 17.03
" Permanganate	$\text{K}_2\text{Mn}_2\text{O}_8$	1200	— 19.18
" Oxalate	$\text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$	800	— 7.41

7. *Sodium Salts.*

Sodium Chloride	NaCl	200	— 1.18
" Bromide	NaBr	200	— 0.15
" Iodide	NaI	200	+ 1.22
" Nitrate	NaNO_3	200	— 5.06
" Sulphate	$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$	400	— 18.76
	Na_2SO_4	400	— 0.06
" Thiosulphate	$\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$	400	— 11.37
" Carbonate	$\text{Na}_2\text{C}_2\text{O}_3 + 10\text{H}_2\text{O}$	800	— 16.49
" Phosphate	$\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$	800	— 22.92
Ammonio-sodic Phosphate	$\text{NaAmHPO}_4 + 4\text{H}_2\text{O}$	800	— 10.75
Sodium Pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$	1600	— 12.06
" Borate	$\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$	2500	— 25.86
" Acetate	$\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$	400	— 4.81

Substance	Formula	Quantity of water in mols.	Thermic effect per mol. of substance
8. Barium Salts.			
Barium Chloride	$\text{BaCl}^2 + 2\text{H}^2\text{O}$	400	- 4.93
" Nitrate	BaN^2O^6	400	- 9.40
" Chlorate	$\text{BaCl}^2\text{O}^6 + \text{H}^2\text{O}$	600	- 11.24
" Dithionate	$\text{CaS}^2\text{O}^6 + 2\text{H}^2\text{O}$	400	- 6.93
" Ethylsulphate	$\text{Ba}(\text{C}^2\text{H}^5\text{SO}^4)^2 + 2\text{H}^2\text{O}$	800	- 4.87
" Acetate	$\text{Ba}(\text{C}^2\text{H}^3\text{O}^2)^2 + 3\text{H}^2\text{O}$	800	- 1.97
" Hypophosphite	$\text{Ba}(\text{PH}^2\text{O}^2) + \text{H}^2\text{O}$	800	+ .29
9. Crystallised Acids.			
Selenious Anhydride	SeO^2	400	- .92
Iodic acid	IO^3H	200	- 2.17
Periodic acid	IO^5H^3	240	- 1.38
Phosphorous acid	PO^3H^3	400	0
Boric "	$\text{B}^2\text{O}^3 + 3\text{H}^2\text{O}$	800	- 10.78
Oxalic "	$\text{C}^2\text{H}^2\text{O}^4 + 2\text{H}^2\text{O}$	500	- 8.56
Succinic "	$\text{C}^4\text{H}^6\text{O}^4$	400	- 6.68
Tartaric "	$\text{C}^4\text{H}^6\text{O}^7$	400	- 3.60
Citric "	$\text{C}^6\text{H}^8\text{O}^7 + \text{H}^2\text{O}$	400	- 6.43
10. Liquid Acids.			
Sulphurous Anhydride	SO^2	300	+ 1.50
Sulphuric "	SO^3	1600	+ 39.17
" 1. Hydrate	$\frac{1}{2}(\text{S}^2\text{O}^7\text{H}^2)$	1600	+ 26.90
" 2. "	SO^4H^2	300	+ 17.85
" 3. "	$\text{SO}^4\text{H}^2 + \text{H}^2\text{O}$	1600	+ 11.58
" with 100 H^2O	$\text{S}^3\text{H}^2 + 99\text{H}^2\text{O}$	1600	+ 1.00
Nitric Acid	NO^3H	20	+ 7.51
Aqueous Nitric Acid	$\text{NO}^3\text{H} + \text{H}^2\text{O}$	320	+ 7.58
	$\text{NO}^3\text{H} + 2\text{H}^2\text{O}$	320	+ 4.28
	$\text{NO}^3\text{H} + 3\text{H}^2\text{O}$	320	+ 2.74
Hydrochloric "	$\text{ClH.H}^2\text{O}$	100	+ 1.83
	$\text{ClH.3H}^2\text{O}$	100	+ 11.68hyp
	$\text{ClH.50H}^2\text{O}$	100	+ 3.82
Acetic "	$\text{C}^2\text{H}^4\text{O}^2$	100	+ .11
		100	+ .15
11. Gaseous Bodies.			
Chlorine	Cl^2	1000	+ 4.87
Hydrogen Sulphide	H^2S	900	+ 4.75
Carbon Dioxide	CO^2	1500	+ 5.88
Sulphur "	SO^2	250	+ 7.69
Nitrogen Tetroxide	NO^2	300	+ 7.75
Ammonia	H^3N	200	+ 8.43
Hydrogen Chloride	HCl	300	+ 17.51
" Bromide	HBr	400	+ 19.94
" Iodide	HI	500	+ 19.21

Most salts, whether anhydrous or hydrated, dissolve in water with absorption of heat; some however, even when united with their maximum amount of crystallisation-water, dissolve with evolution of heat; such is the case with the sulphates of manganese, cadmium, yttrium, lanthanum, and beryllium, the acetates of copper and erbium, and with hypophosphite of barium.

In the amount of heat absorbed in the act of solution there is often an agreement between salts of corresponding formulae: thus the sulphates of magnesium, zinc, nickel, and iron containing 7 mols. water give nearly equal values. To this rule, however, there are conspicuous exceptions; *e.g.* barium nitrate dissolves in water with much greater absorption of heat than the corresponding lead salt, whereas the acetates of the same bases exhibit the opposite relation.

The nitrates and sulphates of the alkali-metals exhibit, for equal numbers of molecules, nearly equal differences of latent heat of solution, *e. g.*—

$\text{R}^{\text{N}}\text{O}^{\text{N}}$	=	K^{N}	Na^{N}	NH^{N}
$\text{R}^{\text{N}}\text{SO}^{\text{N}}$		— 17040	— 10120	— 12640
		— 6380	— 660	— 2370
Difference		— 10660	— 10060	— 10270

Nearly equal differences of latent heat are also found between the nitrates and chlorides of potassium and sodium, but in the ammonia-compounds the difference has a very different value:

RNO^{N}	=	K^{N}	Na^{N}	NH^{N}
RCl^{N}		— 8520	— 5060	— 6320
		— 4440	— 1180	— 3888
Difference		— 4080	— 3880	— 2440

The latent heats of solution of the chlorides, bromides, and iodides of potassium, sodium, and ammonium, likewise do not exhibit any corresponding differences.

Of all salts, the potassium salts exhibit the greatest amount of latent heat for equal numbers of molecules; but the latent heat of sodium salts is much smaller if they contain a considerable amount of water.

All the crystallised acids which have been examined dissolve with absorption of heat, and the same is the case with selenious anhydride. In some, *e. g.* boric acid and the organic acids, the absorption is very considerable. On the contrary, all the liquid acids examined dissolve in water with evolution of heat, which is very great for sulphuric acid, very small for acetic acid.

The latent heat of solution of salts increases with the quantity of water present, so that aqueous solutions of salts, the dissolution of which is attended with absorption of heat, likewise absorb heat on dilution with water. Thus it appears from the numbers above given that a solution of sodium sulphate containing 50 molecules of water absorbs, on dilution with 50, 150, 350, and 550 molecules of water, the following quantities of heat:

n	$(\text{Na}^{\text{N}}\text{SO}^{\text{N}}.50\text{H}^{\text{N}}\text{O}.n\text{H}^{\text{N}}\text{O})$
50	— 0.67 kilogram-degrees
150	— 1.09 "
350	— 1.30 "
550	— 1.35 "

Here the absorption of heat in the dilution of the liquid approximates to a maximum which is more clearly seen from the numbers which exhibit the absorption of heat in such solutions when they are mixed with quantities of water equal to those which they already contain, *e. g.*

n	$(\text{Na}^{\text{N}}\text{SO}^{\text{N}}.n\text{H}^{\text{N}}\text{O}.n\text{H}^{\text{N}}\text{O})$
5	— 0.67 kilogram-degrees
100	— 0.42 "
200	— 0.21 "
400	— 0.06 "

A somewhat different relation is exhibited in the absorption of heat, which takes place when a solution of sodium silicate is diluted with water. Experiment gave the following results:

n	$(\text{Na}^{\text{N}}\text{O}.3\text{SiO}^{\text{N}}.n\text{H}^{\text{N}}\text{O}.n\text{H}^{\text{N}}\text{O})$
37.5	— 0.88 kilogram-degrees
75	— 0.92 "
150	— 0.94 "
300	— 1.17 "
600	— 1.34 "

Hence it appears that, whereas for sodium sulphate the absorption of heat which takes place on diluting the solution with a quantity of water equal to that which it already contains becomes smaller as the quantity of water increases, the contrary is the case with the silicate, so that a solution of the latter containing 300 mols. water exhibits, on dilution with another 300 mols., an absorption of heat $1\frac{1}{2}$ times as great as that which is exhibited by a solution containing only $\frac{1}{3}$ of that quantity of water. In the case of sodium silicate the absorption of heat is very considerable. A solution, which for each mol. $\text{Na}^{\text{N}}\text{O}$ contains 3 mols. SiO^{N} and 37.5 mols. water, exhibits, on dilution with 562.5 mols. water, an absorption of heat amounting to 5.27 kilogram-degrees. This result is probably due to a partial decomposition of the silicate by the action of the water.

In the latent heat of many hydrated salts, the latent heat of the water, *i. e.* of ice, may be recognised. When a salt capable of uniting with water in several proportions

is dissolved in water, the evolution of heat, reckoned absolutely, becomes smaller as the quantity of water contained in the salt is greater. Thus, for example, anhydrous sodium sulphate gives -60 gram-degrees, but the salt containing 10 mols. water gives -18.76 ; cupric sulphate with 1 mol. water gives $+8.72$; the same salt with 5 mols. water gives -2.75 . This difference may arise from two causes; first, the affinity of the salt for the water may not be satisfied in the less hydrated salt, and consequently there may arise an evolution of heat corresponding with the affinity; secondly, the greater absorption of heat which attends the dissolution of the more highly hydrated salt may be due to the passage of a larger quantity of water from the solid to the liquid state. If the affinity between the salt and the water is very small, the effect is due almost entirely to the latter cause. The latent heat of ice at 0° amounts to 1.442 kilogram-degrees; but if the dissolution of the salt takes place at 20° , this amount must be increased by 20 times the difference between the molecular heat of water and that of ice, or about 0.18 kilogram-degree, so that the heat of solution of 1 mol. water (ice) at 20° amounts to about -1.62 kilogram-degrees.

Manganous sulphate crystallises with 4 and 5 mols. water; the affinity of the fifth water-molecule is very small; the difference of the heats of solution amounts, according to the numbers above given, to $.04 - 1.77 = -1.73$ kilogram-degrees.

For sodium phosphate and sodium ammonium phosphate, the heats of solution are as follows:

For $\text{NaNaHPO}_4 + 12\text{H}_2\text{O}$	-22.92 kilogram-degrees
For $\text{Na}(\text{NH}_4)\text{HPO}_4 + 4\text{H}_2\text{O}$	-10.75
Difference for $\text{Na} - \text{NH}_4 + 8\text{H}_2\text{O}$	-12.17 "

Now the difference for the nitrates is $+1.26$; for the sulphates $+\frac{1}{3} 2.31 = +1.155$; mean $+1.208$; hence the latent heat for 8 mols. water is $-12.17 - 1.208 = -13.378$; or for 1 mol. water -1.672 .

A similar magnitude is distinctly recognisable in the heat of solution of sodium carbonate with $10\text{H}_2\text{O}$: for $-1.649 = -0.1649 \times 10$. In sodium sulphate also there is a similar difference between the anhydrous and the hydrated salt, viz. $-18.7 = -1.87 \times 10$.

Heat of Solution of Chlorine-, Bromine-, and Iodine-compounds

(Thomsen, *J. pr. Chem.* [2], xvi. 323-341; *Deut. Chem. Ges. Ber.* x. 1017-1023). The following table exhibits the results of the whole of Thomsen's experiments on the heat of solution of the halogen-compounds of the metals. The numbers are calculated for a temperature of 18° . As it is very difficult and sometimes impossible to bring the amount of water in a hydrated compound into exact agreement with the number of molecules in the formula, inasmuch as some compounds are very deliquescent, and others lose water in drying, the proportion of water (in molecules) as directly determined by analysis is given in the last column.

Radicle	Formula	Mols. of water in solution	Heat of solution	Analysis
Potassium	KCl	200	-4.44	—
	KBr	200	-5.08	—
	KI	200	-5.11	—
Sodium	NaCl	100	-1.18	—
	NaBr	200	-1.19	—
	NaI	200	$+1.22$	—
	$\text{NaBr} + 2\text{H}_2\text{O}$	300	-4.71	2.10 mols.
	$\text{NaI} + 2\text{H}_2\text{O}$	300	-4.01	2.04 "
Lithium	LiCl	230	$+8.44$	—
	BaCl ²	400	$+2.07$	—
Barium	BaBr ²	400	$+4.98$	—
	$\text{BaCl}_2 + 2\text{H}_2\text{O}$	400	-4.93	1.98 "
	$\text{BaBr}_2 + 2\text{H}_2\text{O}$	400	-4.13	2.00 "
	SrCl ²	400	$+11.14$	—
Strontium	SrBr ²	400	$+16.11$	—
	$\text{SrCl}_2 + 6\text{H}_2\text{O}$	400	-7.50	6.00 "
	$\text{SrBr}_2 + 6\text{H}_2\text{O}$	400	-7.20	6.18 "
	CaCl ²	300	$+17.41$	—
Calcium	CaBr ²	400	$+24.51$	—
	CaI ²	400	$+27.69$	—
	$\text{CaCl}_2 + 6\text{H}_2\text{O}$	400	-4.34	6.07 "
Magnesium	MgCl ²	800	$+35.92$	—
	$\text{MgCl}_2 + 6\text{H}_2\text{O}$	400	$+2.95$	6.11 "

Chlorides, Bromides, and Iodides.

Radicle	Formula	Mols. of water in solution	Heat of solution	Analysis
Aluminium . . .	$AlCl^3$	25.0	+ 153.69	—
Zinc	$ZnCl^2$	3.0	+ 15.63	—
	$ZnBr^2$	400	+ 15.03	—
	ZnI^2	400	+ 11.31	—
	$CdCl^2$	400	+ 3.01	—
Cadmium	$CdBr^2$	400	+ .44	—
	CdI^2	400	— .96	—
	$CdCl^2 + 2H^2O$	400	+ .76	2.10 mols.
	$CdBr^2 + 4H^2O$	600	— 7.29	4.06 "
Manganese . . .	$MnCl^2$	350	+ 16.01	—
	$MnCl^2 + 4H^2O$	400	+ 1.54	3.88 "
Iron	$FeCl^3$	2000	+ 63.36	—
	$FeCl^2$	350	+ 17.90	—
	$FeCl^2 + 4H^2O$	400	+ 2.75	—
Cobalt	$CoCl^2$	400	+ 18.34	—
	$CoCl^2 + 6H^2O$	400	— 2.85	5.80 "
Nickel	$NiCl^2$	400	+ 19.17	—
	$NiCl^2 + 6H^2O$	400	— 1.16	6.02 "
Copper	$CuCl^2$	600	+ 11.08	—
	$CuBr^2$	400	+ 8.25	—
	$CuCl^2 + 2H^2O$	400	+ 4.17	1.99 "
Lead	$PbCl^2$	1800	— 6.80	—
Thallium	$PbBr^2$	2500	— 10.04	—
	$TlCl^2$	9000	— 20.20	—
Mercury	$HgCl^2$	300	— 3.30	—
	$HgCl^2K^2 + H^2O$	680	— 16.39	—
	$HgBr^2K^2$	660	— 9.75	—
	HgI^2K^2	800	— 9.81	—
Phosphorus . . .	PCl^3	1600	+ 65.14	—
Arsenic	$AsCl^3$	450	+ 17.58	—
Antimony	$SbCl^3$	900	+ 8.37	—
	$AuCl^3$	900	+ 4.45	—
Gold	$AuBr^3$	2000	— 3.76	—
	$AuCl^3 + 2H^2O$	600	— 1.69	2.10 "
	$AuCl^3H + 3H^2O$	450	— 5.85	3.65 "
	$AuBr^3H + 5H^2O$	1000	— 11.40	5.28 "
Tin	$SnCl^2$	300	+ .35	—
	$SnCl^4$	300	+ 29.92	—
	$SnCl^2 + 2H^2O$	200	— 5.37	—
	$SnCl^2K^2 + H^2O$	600	— 13.42	—
	$SnCl^2K^2$	800	— 3.88	—
Titanium	$TiCl^4$	1300	+ 57.87	—
Silicon	$SiCl^4$	3000	+ 69.26	—
Palladium	$PdCl^2K^2$	800	— 13.63	—
	$PdCl^2K^2$	—	— 15	—
	$PtCl^2K^2$	600	— 12.22	—
	$PtCl^2Am^2$	600	— 8.48	—
Platinum	$PtBr^2K^2$	800	— 10.63	—
	$PtCl^2K^2$	—	— 13.76	—
	$PtBr^2K^2$	2000	— 12.26	—
	$PtCl^2Na^2 + 6H^2O$	900	— 10.63	5.98 "
	$PtBr^2Na^2 + 6H^2O$	800	— 8.55	6.05 "
	$PtCl^2Na^2$	800	+ 8.54	—
	$PtBr^2Na^2$	600	+ 9.99	—
Hydrogen	HCl	300	+ 17.31	—
	HBr	400	+ 19.94	—
	HI	500	+ 19.21	—
	NH^4Cl	200	— 3.88	—
Ammonium	NH^4Br	200	— 4.38	—
	NH^4I	200	— 3.55	—
Hydroxylamine . .	NOH^4Cl	200	— 3.65	—
Platodiamine . . .	$Pt^4NH^4Cl^2 + H^2O$	400	— 8.76	—
Triethylsulphine .	$SC^6H^{15}I$	267	— 5.75	—

The anhydrous chlorides, bromides, and iodides dissolve in water either with evolution or with absorption of heat, aluminium chloride showing the greatest evolution, and thallium chloride the greatest absorption.

The anhydrous chlorides, bromides, and iodides, which dissolve in water with evolution of heat, form crystalline compounds with water.—To this group belong the haloid compounds of Li, Ba, Sr, Ca, Mg, Al, Zn, Mn, Fe, Co, Ni, Cu, Sn. The heat of solution of the anhydrous chloride and bromide of cadmium is positive, and both bodies combine with water; cadmium iodide, on the other hand, has a negative value, and this body does not combine with water at ordinary temperatures. The heat of solution of the anhydrous chloride of gold, AuCl_3 , is positive; that of the bromide, AuBr_3 , negative; the former combines with water to produce the compound $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$; the latter forms no hydrate. Sodium iodide shows a positive value, and crystallises in combination with water; the value for the bromide is almost nil, and the hydrate is easily decomposed; that of the chloride is negative, and it combines with water at a very low temperature only.

The hydrated chlorides, bromides, and iodides generally absorb heat on solution in water, but the following are exceptions: $\text{MgCl}_2 + 6\text{H}_2\text{O}$, $\text{MnCl}_2 + 4\text{H}_2\text{O}$, $\text{FeCl}_2 + 4\text{H}_2\text{O}$, $\text{CdCl}_2 + 2\text{H}_2\text{O}$, and $\text{CuCl}_2 + 2\text{H}_2\text{O}$. It is not unlikely that compounds of these bodies with a larger proportion of water are possible.

The heat of formation of hydrates is positive, the evolution of heat being due, partly to the latent heat of water, and partly to the affinity of the haloid compound for water, and its value depends on the number of molecules of water taken up.

The magnitude of the heat of solution of the anhydrous haloid compounds appears to be subject to several laws.—In the case of the metals of the alkaline earths, the heat of solution increases with the increasing atomic weight of the electronegative constituent, the chloride evolving least, the iodide most heat. At the same time the heat of solution rises regularly from barium to magnesium, i.e. with the decreasing atomic weight of the electro-positive constituent.

The group of the alkali-metals shows a similar behaviour; but potassium, and probably thallium, form compounds in which the value decreases with the electronegative element, and this is probably connected with the fact that these two metals do not form hydrated haloid compounds.

A comparison of the two groups exhibits some remarkable relations: thus the difference of the heat of solution

between	BaCl_2	and	Ti^2Cl^2	=	22.27
"	SrCl_2	"	K^2Cl^2	=	20.02
"	CaCl_2	"	Na^2Cl^2	=	19.77
"	MgCl_2	"	Li^2Cl^2	=	19.04

The compounds of the formula R^2Cl^2 also show that the heat of solution for equivalent quantities is greater in proportion as the atomic weight of the electro-positive constituent is less.

The heat of solution of the haloid compounds of the heavy metals exhibits the reverse of the above cases: for the quantity is greatest for the chlorides, and least for the iodides.

Heats of Solution of Alkaline Chlorides and Nitrates. Winkelmann (*Pogg. Ann.* cxlix. 1–32) has determined the heats of solution of the chlorides and nitrates of potassium, sodium, and ammonium at the temperatures 0° and 50° , and the specific heats of the resulting solutions. In the following table, k denotes the specific heat; λ_0 and λ_{50} the quantities of heat required to dissolve 1 gram of the salt at the respective temperatures; p the percentage in grams of salt contained in the solution.

Sodium Chloride.

$$\begin{aligned} k &= 0.99608 - 0.01079 p + 0.000137 p^2. \\ \lambda_0 &= 32.1 - 1.837 p + 0.0687 p^2, \text{ up to } p = 11.2. \\ \lambda_0 &= 28.62 - 0.8475 p + 0.00791 p^2, \text{ from } p = 11.2 \text{ to } p = 32.04. \\ \lambda_{50} &= 6.41 - 0.07 p, \text{ from } p = 3.09 \text{ to } p = 26.03. \end{aligned}$$

Sodium Nitrate.

$$\begin{aligned} k &= 1.0015 - 0.01066 p + 0.000161 p^2, \text{ from } p = 3.03 \text{ to } p = 19.10. \\ k &= 0.9410 - 0.004 p, \text{ from } p = 25.03 \text{ to } p = 40.06. \\ k &= 0.8703 - 0.002233 p, \text{ from } p = 40.06 \text{ to } p = 70.09. \\ \lambda_0 &= 64.4 - 0.728 p, \text{ from } p = 3.03 \text{ to } p = 23.6. \\ \lambda_0 &= 58.1 - 0.5221 p + 0.002644 p^2, \text{ from } p = 23.6 \text{ to } p = 70.0. \\ \lambda_{50} &= 51.1 - 0.3037 p, \text{ from } p = 3.03 \text{ to } p = 31.3. \\ \lambda_{50} &= 45.1 - 0.123 p, \text{ from } p = 31.3 \text{ to } p = 70. \end{aligned}$$

Potassium Chloride.

$$\begin{aligned} k &= 0.9965 - 0.011491 p + 0.0001086 p^2, \text{ from } p = 3.04 \text{ to } p = 29.4. \\ \lambda_0 &= 69.48 - 0.75 p, \text{ from } p = 3.04 \text{ to } p = 49.6. \\ \lambda_0 &= 65.4 - 0.34 p, \text{ from } p = 9.6 \text{ to } p = 29.4. \\ \lambda_{30} &= 45.3 - 0.1 p, \text{ from } p = 3.0 \text{ to } p = 29.4. \end{aligned}$$

Potassium Nitrate.

$$\begin{aligned} k &= 0.9979 - 0.01039 p + 0.000143 p^2, \text{ from } p = 3.05 \text{ to } p = 19.80. \\ \lambda_0 &= 95.9 - 2.123 p, \text{ from } p = 3.05 \text{ to } p = 5.6. \\ \lambda_0 &= 85.64 - 0.161 p - 0.0246 p^2, \text{ from } p = 5.62 \text{ to } p = 19.8. \\ \lambda_{30} &= 73.66 - 0.42 p, \text{ from } p = 3.0 \text{ to } p = 19.8. \end{aligned}$$

Ammonium Chloride.

$$\begin{aligned} k &= 0.9962 - 0.01114 p - 0.000132 p^2, \text{ from } p = 3.03 \text{ to } p = 25. \\ \lambda_0 &= 85.66 - 0.357 p - 0.0192 p^2, \text{ from } p = 3.0303 \text{ to } p = 9.98. \\ \lambda_0 &= 78.26 + 0.387 p - 0.0287 p^2, \text{ from } p = 9.98 \text{ to } p = 25. \\ \lambda_{30} &= 55.1 + 0.1 p, \text{ from } p = 3.03 \text{ to } p = 25. \end{aligned}$$

Ammonium Nitrate.

$$\begin{aligned} k &= 0.9835 - 0.00618 p, \text{ from } p = 3.04 \text{ to } p = 20. \\ k &= 0.7925 + 0.008555 p - 0.0002575 p^2, \text{ from } p = 20 \text{ to } p = 40. \\ \lambda_0 &= 92.25 - 1.737 p + 0.04025 p^2, \text{ from } p = 3.04 \text{ to } p = 20. \\ \lambda_0 &= 89.1 - 0.985 p + 0.0105 p^2, \text{ from } p = 20 \text{ to } p = 40. \end{aligned}$$

The values of the specific heats of nitrate and chloride of ammonium are not so well established as the rest.

Winkelmanna's determinations do not exhibit any general simple relation between the heat of solution and the quantity of water required to dissolve the salt.

Cold produced by Solution of Ammonium Nitrate in Water (J. Tollinger, *Wien. Akad. Ber.* [2 Abth.] lxxii. 535-577). The specific heat of a solution of 1 mol. of the salt in 100 mols. water, or of 1 part by weight of the salt in 22.5 parts by weight of water, is 0.95955 between 20° and 27°, or nearly 0.962 for ordinary temperature. Thomsen found 0.962; Winkelmanna 0.956. The general expression for the molecular heat of 1 mol. of the salt in m mol. water is—

$$S_m = \frac{736 + 354.8 m + 48 m^2}{20 + m};$$

or more simply for $m < 8$, $S_m = 29.6 + 17.7m$; for $m > 8$, $S_m = 20 + 17.8m$. The specific heat of the solid salt is, according to previous determinations by Tollinger, 0.429 (*ibid.* lxi. 319; *Jahresb. f. Chem.* 1870, 112). The estimation of the heat of solution at different temperatures* led, for the unit of weight, and for the molecule (80) to the equations:

$$w_t = 84.23 - 0.408 t \text{ and } W_t = 6738 - 32.6 t.$$

The quantity of heat absorbed in the solution of 1 mol. of the salt in m mol. water at the temperature t is represented by the general equation—

$$W_{mt} = \frac{25342}{9 + m} + \frac{7091 m}{20 + m} - t \frac{39.6 m + 48}{20 + m}.$$

For the point of solidification τ , the determinations above given lead to the following equations:

$$\tau = -0.338 p - 0.0015 p^2, \text{ or } \tau = -\frac{149}{2.7} + \frac{0.5 m}{m},$$

in which p denotes the percentage of salt and m , as before, the number of molecules of H₂O to 1 mol. NH₄NO₃.

With respect to the solubility of the salt, the investigations relating to the determination of the point of saturation give the equations—

$$\vartheta = -88.5 + 1.64 p; \text{ and } \vartheta = \frac{335.5 - 88.5 m}{4.44 + m}.$$

The attainable minimum of temperature is limited by the points of solidification and

* Compare Winkelmanna, *supra*, and Thomsen, p. 987 of this Supplement.

saturation, therefore by τ and β , for both of which, according to the formulæ above given, $m=5.82$. Substituting this value, we find

$$\tau = \beta = -17.59.$$

The most favourable proportion of a mixture for cooling a body down to a given temperature corresponds with that degree of concentration which just gives the saturation at the desired final temperature. For the practical application of mixtures of water or snow with ammonium nitrate as frigorific mixtures, Tollinger has calculated two tables according to the points of view above indicated. When snow is used, the molecular heat of fusion = 1440 gram-degrees, and the molecular heat, 34, of ice, likewise enter into the calculation.

• **Heat of Solution and Dilution of Nitric Acid.** The following table contains the results of two series of experiments by Thomsen (*Dent. Chem. Ges. Ber.* vi. 697), in the first of which a hydrate of nitric acid containing α -molecules of water was mixed with the quantity of water required to make up 100 molecules, that is to say with 100 α -molecules of water; in the second series the acid was each time mixed with a quantity of water equal to that which it already contained, that is to say, with α -molecules:

α	$[\text{NO}^3\text{H} \cdot \alpha \text{H}^2\text{O}, (100-\alpha)\text{H}^2\text{O}]$	α	$\text{NO}^3\text{H} \cdot \alpha \text{H}^2\text{O}, \alpha \text{H}^2\text{O}$
0.175	6.650 kil.-deg.	0.3125	1.014 kil.-deg.
0.5	5.458 "	0.625	1.393 "
1.0	4.171 "	1.25	1.556 "
1.5	3.292 "	2.5	1.378 "
2.5	2.146 "		
3.0	1.720 "		
5.0	0.758 "		

From these values Thomsen draws the following conclusions: When a hydrated nitric acid $\text{NO}^3\text{H} \cdot \alpha \text{H}^2\text{O}$ is mixed with a quantity of water equal to that which it already contains, the evolution of heat at first increases with α till α becomes equal to 1.244, at which point the quantity of heat evolved attains its maximum value, viz. 1.556 kilogram-degrees. When the acid becomes weaker, that is, when $\alpha > 1.234$, the evolution of heat diminishes, and when the acid contains 20 mols. water it changes to absorption; in other words, the thermic effect becomes negative. The absorption of heat on mixing the acid with water goes on till the acid contains 40 molecules of water, but on continuing the dilution, evolution of heat again takes place. The minimum of heat-evolution on mixing aqueous nitric or sulphuric acid with a quantity of water equal to that which it already contains, takes place at that degree of dilution of the acid at which the molecular heat (or calorimetric equivalent) of the acid is equal to that of the water contained in it. For hydrochloric acid this last statement does not hold good, because in solutions of this acid the calorimetric equivalent of the acid is always less than that of the water with which it is associated.

The following values, true for the temperature 9.7° , are deduced by interpolation from the results of experiments by Berthelot (*Compt. rend.* lxxviii. 769-777).

Formula of the original acid,	Evolution of Heat on dilution to $\text{NO}^3\text{H} + 200 \text{H}^2\text{O}$
$\text{NO}^3\text{H} + \alpha \text{H}^2\text{O}$	
NO^3H	7.15 kil.-degrees.
$\text{NO}^3\text{H} + 0.5 \text{H}^2\text{O}$	5.15 "
1.0	3.84 "
1.5	3.02 "
2	2.32 "
3	1.42 "
4	0.79 "
5	0.42 "
6	0.20 "
7	0.06 "
7.5	0 "
8	-0.04 "
10	-0.09 "
15	-0.24 "
20	-0.18 "
40	-0.09 "
$100 \text{H}^2\text{O}$	-0.03 "

From these results, Berthelot infers the existence of the hydrate $\text{NO}^3\text{H}\cdot 2\text{H}^2\text{O}$. He regards as incorrect the statement of Thomsen that the absorption of heat which takes place on diluting the acid with water changes to evolution of heat at certain degrees of hydration. The influence of temperature is deducible from the formula $Q_r = Q_s + U - V$, and while $\text{NO}^3\text{H} + n\text{H}^2\text{O}$ is increasing to $\text{NO}^3\text{H} + 200\text{H}^2\text{O}$, n is less than 200, and consequently U greater than V , so that the heat of dilution increases continually with the temperature. The experiments of Hesse, Thomsen, and Berthelot on the specific heats of these solutions, give for

$$\begin{aligned} n = 0 : U - V &= 0.040 \left(\frac{1}{t} - t \right); \quad n = 10 : U - V = 0.0181 (\tau - t) \\ n = 20 : U - V &= 0.0116 (\tau - t); \quad n = 40 : U - V = 0.0051 (\tau - t) \\ n = 80 : U - V &= 0.001 (\tau - t). \end{aligned}$$

The molecular volumes of nitric acid solutions are represented approximately by the formula

$$V = 18n + 29 + \frac{39}{n + 3.2}.$$

Thermic Effects of the Reaction of Sulphuric Acid with Water.

Thomsen (*Ber.* vi. 496) regards the greater number of the experiments hitherto made by himself and others (*2nd Suppl.* 633) on the evolution of heat attending the mixing of sulphuric acid with water, as deficient in accuracy, and has therefore undertaken new experiments, in which, for all determinations of large numbers, he used 49 grams of strong sulphuric acid, SO^4H_2 , or about a hundred times the quantity employed by Favre et Silberman. Two series of experiments were made, as in the case of nitric acid, a hydrate containing $a\text{H}^2\text{O}$ being diluted in the first series with $(100-a)\text{H}^2\text{O}$; and in the second with $a\text{H}^2\text{O}$. All the hydrates were analysed with the greatest care, so as to preclude as far as possible an error of 1 per thousand in their numbers of water-molecules. The following table exhibits the results.

a	$\text{SO}^4a\text{H}^2\text{O}, (100-a)\text{H}^2\text{O}$	a	$\text{SO}^4a\text{H}^2\text{O}, a\text{H}^2\text{O}$
1	16.850 kil.-degrees	50	174 kil.-degrees
2	10.578 "	100	206 "
3	7.486 "	200	248 "
4	5.742 "	400	328 "
6	3.768 "	800	216 "
10	1.910 "		
20	.692 "		
30	.174 "		

From these values Thomsen calculates the quantities of heat evolved on mixing 1 mol. sulphuric acid, SO^4H_2 , with n molecules of water. The results are given in the following table:—

n	Heat evolved in the formation of $\text{SH}^2\text{O}^4a\text{H}^2\text{O}$	n	Heat evolved in the formation of $\text{SO}^4\text{H}_2\cdot a\text{H}^2\text{O}$
1	6.272 kil.-degrees	49	16.676 kil.-degrees
2	9.364 "	99	16.850 "
3	11.108 "	199	17.056 "
5	13.082 "	399	17.304 "
9	14.940 "	799	17.632 "
19	16.248 "	1599	17.848 "

Pfaundler (*Wien. Acad. Ber.* [2 Abth.], lxxi. 155–178) has repeated his measurements of the heat evolved on mixing sulphuric acid with water, with results approaching very nearly to those formerly obtained (*2nd Suppl.* 634). Denoting by n the number of water-molecules added to sulphuric acid SO^4H_2 , the quantities of heat evolved in the formation of the several hydrates from 1 gram of SO^4H_2 may be approximately represented within the limits $n=1$ and $n=5$ by the formula

$$W_n = \frac{n}{n + 1.588} \cdot 17.92.$$

The rise of temperature t produced in the formation of the several hydrates is shown in the following table:

n	t	corrected	n	t	t corrected
0.5	89.0°	82°	4	138.7°	133°
1	134.2	127	5	125.1	121
1.5	151.2	145	5	111.9	109
2	158.4	152	7	99.3	98
2.5	155.4	149	8	91.2	89
3	153.3	145	9	83.8	81
3.5	145.9	140	10	77.0	76

The calculation of t is based on the specific heat of the hydrates at ordinary temperatures, that of t corrected, on the specific heat as it increases with the temperature between 0° and 159°.

The greatest rise of temperature amounts to 159°, and is obtained on mixing 1 mol. SO_4H_2 with 1.84 mol. H_2O , or 1 part by weight of SO_4H_2 with 0.338 part water.

Berthelot (*Compt. rend.* lxxviii. 716) has investigated the thermic relations of the crystalline hydrate of sulphuric acid, $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$, with the following results:

$\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$ solid + 400 H_2O evolves	Kil.-degrees
$\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$ liquid + 400 H_2O "	0.712
Whence the heat of fusion of $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$	10.80
SO_4H_2 liquid + H_2O liquid = $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$ liquid, 16920—10800	= 0.368*
SO_4H_2 solid + H_2O solid = $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$ solid, 16060—7120—1440	= 0.612
	= 0.750

The existence of the hydrate $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$ may be inferred, according to Berthelot, from its thermic relations. For, as appears from the experiments of Favre and Quatillard (*2nd Suppl.* 633), on mixing 1 mol. SO_4H_2 successively with $\frac{1}{2}$, $\frac{1}{4}$ &c. mol. water, the quantities of heat evolved are proportional to the quantities of water added up to 1 mol. H_2O , whereas above that limit they decrease rapidly. The variations in the heat-capacities and vapour-tensions tend also to the same conclusion.

Thomsen, on the other hand (*Ber.* vii. 772), regards the existence of definite hydrates in the aqueous solutions of acids as not satisfactorily established. With regard to the hydrate of sulphuric acid, $\text{SO}_4\text{H}_2 \cdot \text{H}_2\text{O}$, the proportionality maintained by Berthelot of the quantities of heat evolved on mixing 1 mol. SO_4H_2 with fractions of a molecule of water is not borne out by the experiments of Favre and Quatillard above cited, or by his own. With regard also to the hydrate of nitric acid, $\text{NO}_3\text{H} \cdot 2\text{H}_2\text{O}$, Berthelot's determination of the quantities of heat evolved on mixing nitric acid with water are not convincing, and on the other hand, Thomsen's own experiments show a continuous evolution of heat up to 5 H_2O , and therefore give no indication whatever of the existence of a hydrate $\text{NO}_3\text{H} \cdot 2\text{H}_2\text{O}$.

Thermic Changes attending the Solution of Chlorine in Water, and the Oxidation of various Salts by Chlorine. Berthelot (*Compt. rend.* lxxvi. 1514—1522; *Ann. Chim. Phys.* [5], v. 318—356) finds that the heat of solution of chlorine in water varies between 1.64 and 3.77 kil.-degrees, and considers that the variation is due, not to the existence of two allotropic states of the gaseous chlorine, but to the circumstance that the chlorine is sometimes simply dissolved by the water, and sometimes acts chemically on it, the action being exerted both on the hydrogen and on the oxygen. The decomposition of water by chlorine, with evolution of free oxygen ($\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}_2$) should evolve 10 kilogram-degrees of heat. The formation of hydrochloric acid and the oxides of chlorine appears to be induced by the presence of a small quantity of a foreign body, perhaps a trace of hypochlorous acid.

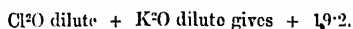
Similar irregularities are observed in the oxidation of mercurous chloride, stannous chloride, and ferrous sulphate by the agency of chlorine. Thus, in the action of chlorine-water on calomel, the heat evolved varies, for 35.5 grams of chlorine, between +16.3 and +22.8 kilogram-degrees; in the action on neutral stannous chloride between +36.5 and +39.6, becoming constant however and equal to +32.2 in presence of a certain quantity of hydrochloric acid; on neutral ferrous sulphate, between 20.44 and 23.87, becoming constant and = 26.65 in presence of a molecule of sulphuric

* This number is considerably greater than the heat of fusion of the pure acid, SO_4H_2 , viz. 0.86, and greater even than the sum of the heats of fusion of the acid and water, viz. $0.86 + 1.44 = 2.3$.

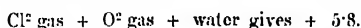
acid, SO_4H^2 , and rising to 27.39 in presence of $2\text{SO}_4\text{H}^2$. These thermal variations may be explained on the assumption that, in the oxidation of the preceding salts, the chlorine first decomposes the water and produces oxides of chlorine, with evolution of a smaller amount of heat for an equal weight of chlorine. These oxides of chlorine however disappear in course of time, and bring about the same final condition, *e.g.* the formation of stannic chloride, SnCl_4 , but so slowly that the heat thereby evolved is not indicated by the thermometer. In presence of a large excess of dilute hydrochloric acid, the quantity of heat evolved becomes nearly constant, *e.g.* in the case of stannous chloride 38.5 kil.-deg. for 35.5 grm. chlorine. The action of chlorine on alkaline oxides gives constant quantities of heat:

For Cl^2 and K^2O	+ 25.4
" Cl^2 " Na^2O	+ 25.3
" Cl^2 " BaO	+ 25.0

On the other hand



Therefore



In view of the irregularities above noticed, Berthelot is of opinion that calorimetric determinations, like those of Thomsen (p. 961), depending on oxidising actions under the influence of chlorine, are not to be depended upon. Free hypochlorous acid cannot be used for a similar purpose excepting in cases where the oxidation is very quickly completed. *Potassium permanganate* also cannot be safely used for thermo-chemical investigations. On the whole, the use of indirect oxidation and reduction in thermo-chemistry requires very great caution.

Thermic changes accompanying the action of the Haloid Acids in Aqueous Solution on the Oxides of Potassium, Mercury, and Silver; also the mutual displacement of these Acids from their Salts (Berthelot, *Compt. rend.* lxxvii. 308):

				Kil.-deg.
2HCl (in 4 litres)	+	K^2O (in 4 litres)	.	+ 27.18
2HBr "	+	K^2O "	.	+ 27.60
2HI "	+	K^2O "	.	+ 27.16
HI (in 2 litres)	+	KCl (in 2 litres)	.	+ 0.04 } diff.
HCl "	+	KI "	.	+ 0.10 } - 0.06
HCl gas + water (800H ² O)		+ 17.43	KCl solid + water	- 4.19
HBr "		+ 20.00	KBr "	- 5.45
HI "		+ 19.57	KI "	- 5.32
HgCl ² (in 12 l.)	+	K^2O (in 4 l.)	.	+ 8.34
HgCl ² (in 16 l.)		" "	.	+ 8.18
HgCl ² (solid)	+	water (40 pts.)	.	- 3.04
whence HgO + 2HCl (dilute)	=	HgCl ² dissolved	.	+ 18.92
" "	=	" solid	.	+ 21.96
HgCl ² (in 8 l.) + 2KI (in 8 l.)	=	HgI ² (ppt.) + 2KCl (diss.)	.	+ 41.02
If the quantity of mercuric iodide dissolved be taken into account, the last number becomes 41.32, whence:				
HgO + 2HI dilute	=	HgI ² solid	.	+ 60.24
NO^3Ag (in 6 l.) + KCl (in 2 l.)	.	.	.	+ 15.67
2NO ³ H dilute + K^2O dilute	.	.	.	+ 27.66
2NO ³ Ag (in 4 l.) + K^2O (in 4 l.)	.	.	.	+ 17.32
whence 2NO ³ H dilute + Ag ² O precipitated	.	.	.	+ 10.34
2HCl "	+	" "	.	+ 41.20
2HCl gas + " "	=	2AgCl + H ² O gas	.	+ 56.8
The last figure, however, is only approximately correct, inasmuch as the physical state of silver chloride, as shown by Stas, varies with the conditions of precipitation and more especially of drying; the same is true for silver oxide.				
NO^3Ag (in 6 l.) + KBr (in 2 l.)	.	.	.	+ 20.30
whence 2HBr dilute + Ag ² O = 2AgBr precipitated	.	.	.	+ 50.28
2HBr gas + " "	=	" "	+ H ² O gas	+ 71.0 (approx.)
NO^3Ag (in 6 l.) + KI (in 4 l.)	.	.	.	+ 26.90
whence 2HI dilute + Ag ² O = 2AgI precipitated	.	.	.	+ 63.64
" gas + " "	=	" "	+ H ² O gas	+ 83.6 (approx.)

A comparison of these numbers shows that the mutual displacement of the halogens does not in general produce any thermal effects which can be regarded as constant, or at all events as multiples of a common constant. An approximately constant relation exists, however, for the salts of the alkali-metals, and for the acid chlorides, bromides, and iodides of certain non-metallic elements, and of certain organic compounds analogous in constitution to the haloïd acids.

The partition of an alkaline base, potash for example, between two haloïd acids, cannot be predicted on thermochemical grounds, since the quantities of heat evolved in the formation of the alkaline chlorides, bromides, and iodides are equal. In this case opposite reactions may take place accordingly as the solution is evaporated or precipitated. An excess of hydriodic acid expels the other two acids almost completely on evaporation; and hydrochloric acid is almost wholly expelled by an excess of hydrobromic acid; but the displacements are not complete when the acids are present in equivalent quantities. On the contrary, hydrochloric acid, even in considerable excess, displaces only a fraction of an equivalent of hydrobromic acid. A strong solution of hydrochloric acid added to a saturated solution of potassium iodide produces a crystalline precipitate of potassium chloride, containing only traces of iodine. Berthelot considers that in this case the hydrochloric acid first divides the base with the hydriodic acid, and that the anhydrous hydrochloric acid, which, according to Berthelot, is always present in concentrated solutions, lays hold of the water which holds the potassium chloride in solution, and precipitates the latter.

Berthelot has also observed the following reaction: $\frac{\text{HgCl}^2}{2}$ (1 eq. in 4 l.) + KI (1 eq. in 4 l.) develops 13.67 and 13.61 kil.-deg. of heat instead of 20.6: consequently III dissolved + $\frac{\text{HgO}}{2}$ precipitated gives 23.0. Between the formation of solid mercuric chloride and that of the solid iodide by means of the dissolved haloïd acids, there is, therefore, a thermal difference of 12.1, whereas for potassium iodide and chloride it amounts to only 1.1, and rises for silver iodide to 11.2, which number would fall back to 8.4 if the observation were made at the first moment of precipitation. The formation of mercuric iodide surpasses, therefore, in a thermal point of view, that of all other known iodides.

Formation of Cyanides (Berthelot, *Compt. rend.* lxxvii. 338). See also 2nd Suppl. 662:

	Heat-units
2HCy (in 4 l.) + HgO (suspended in 20 l.)	+ 30.96
HgCy solid + water (40 pts.) = solution	- 1.50
HCy gas, liquefied by pressure	+ 5.70
HCy liquid + water (large quantity)	+ 6.40

whence:

2HCy dissolved + HgO = HgCy ² solid	+ 34.0
2HCy liquid + HgO = HgCy ² „	+ 34.8
2HCy gas + HgO = HgCy ² „ + H ₂ O gas	+ 36.6

The formation of dissolved mercuric cyanide develops +12.06 more than that of mercuric chloride, and consequently mercuric chloride in dilute solution is completely decomposed by hydrocyanic acid. Experiment gave:

HgCy ² (in 32 l.) + 2HCl (in 4 l.)	+ 0.0	N - N ₁ * = 11.8
HgCl ² „ + 2HCy „	+ 11.8	calc. = 12.0

On the contrary, dissolved potassium cyanide is completely decomposed by dilute hydrochloric acid.

2HCy dissolved + K ₂ O dilute	+ 5.92	} N ₁ - N = 12.0
2HCl „ + „	+ 27.18	

Strong hydrochloric acid, on the other hand, decomposes mercuric cyanide, the decomposition being due, according to Berthelot, to the action of the anhydrous hydrogen chloride, which is either contained in the solution, or produced under the influence of heat, and exhibits, for 1 mol., an amount of energy exceeding that of the hydrated acid by 6 or 7 heat-units. Gaseous hydrogen chloride expels gaseous hydrogen cyanide from mercuric cyanide at ordinary temperature with evolution of 5.2 heat-units for 1 mol. of the acid.

Berthelot has also observed the following developments of heat:

2KCy (in 16 l.) + HgCl ² (in 8 l.)	+ 33.4
2KCl „ + HgCy ² „	0

* N stands for heat of neutralisation (2nd Suppl. 628).

By calculation, $(N - N_1) - (N' - N'_1) = 13.6 - 3.0 - (9.5 - 15.5) = +16.6$ for 1 mol. acid, and for the above 2 mols., $2 \times 16.6 = 32.2$.

The following is a marked exception to the law of thermoneutrality of salts (p. 985), a double cyanide being formed, and the dissolution being attended with considerable evolution of heat:

HgI ² solid	+ 2KCy (in 34 l.)	+ 9.4
	+ 2KCy	+ 9.4
Total heat of solution			18.8

This formation of double cyanides is shown still more clearly by the following experiment:

HgCy ² (in 32 l.)	+ 2KCy (in 8 l.)	+ 11.6
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Dilute hydrochloric acid added to the preceding liquid forms KCl and HCy:

Preceding liquid	+ HCl (in 2 l.)	+ 5.2
	+ 2HCl	—

The following experiments were made with silver cyanide:

(1) NO ³ Ag (in 16 l.)	+ HCy (in 4 l.)	+ 15.72
from which			
2HCy dissolved	+ Ag ² O = 2AgCy precipitated	+ 11.8
(2) NO ³ Ag (in 16 l.)	+ KCy (in 4 l.)	+ 26.57
whence			
2HCy dissolved	+ Ag ² O = 2AgCy precipitated	+ 41.8

Consequently

2HCy liquid	+ Ag ² O precipitated	= 2AgCy + H ² O liquid	42.6
" gas	+	"	= " + "	51.6
" "	+	"	= " + "	44.4

Further, the formation of a double cyanide gave:

KCy (in 4 l.)	+ AgCy precipitated	+ water (20 l.)	5.6
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Heat of Solution of the Alkalis and Alkaline Earths (Berthelot, *Compt. rend.* lxxvi. 1041, 1106). KHO (56.1 grams) in dissolving in 260 molecules of water gives out 12.46 kil.-degrees of heat; commercial pure potash containing KHO + 0.88H²O gave off only 4.60; the pure crystallised hydrate KHO.2H²O gave -0.03. The quantities of heat evolved in the dilution of potash-solution, KHO.nH²O, may be represented by the formula $A = \frac{23}{n^2}$, as far as $n = 11$; above that limit, the term

$-\frac{23}{10n}$ must be appended; for values of n above 32 the formula is reduced to this latter term, and on further dilution heat is invariably absorbed.

The heat of solution of NaHO amounts to +9.78 kil.-degrees; for NaHO + 0.76H²O to +7.31. The heat evolved on dilution of soda-solutions, NaHO.nH²O, is represented by the formula $A = \frac{23}{n^2}$, as far as $n = 5.6$; for values of n between 5.6 and 18.4

a correction of -0.60 must be made, and above 18.4 a further correction of $-\frac{23}{2n}$. The molecular volumes of soda-solutions decrease gradually, the limit of this contraction not being reached even at 200H²O. The volume of dilute soda-solutions is smaller than that of the water which they contain.

Ammonia, NH³, in dissolving, evolves 8.82 kil.-degrees. The quantity of heat given off in the dilution NH³.nH²O with 200 H²O is represented by the formula $A = \frac{1.27}{n}$. One volume of water at -16° dissolves 1270 vols. NH³. The molecular volume of the solution NH³ + nH²O is expressed generally by the formula $V = 18n + 24 - \frac{1.2}{n}$.

The quantities of heat evolved in the formation of the hydrates of CaO, BaO, and SrO, and the heats of solution of these hydrates, were deduced from the heat of solution in dilute hydrochloric acid.

Kil.-deg. Kil.-deg. Kil.-deg.
 $\text{CaO} + \text{H}_2\text{O} \dots +15\cdot10$; $\text{BaO} + \text{H}_2\text{O} \dots +17\cdot62$; $\text{SrO} + \text{H}_2\text{O} \dots +17\cdot20$.

The dissolution of the anhydrous bases in water gives rise to the following quantities of heat:

CaO conc. solution	+	18·10;	dilute solution	+	19·00
BaO „ „	+	27·88;	„ „	+	28·12
SrO „ „	+	26·80;	„ „	+	26·8

Thence may be deduced for the heats of solution of the three hydrates the numbers $+3\cdot0$, $+10\cdot26$, $+9\cdot64$. In the formation of the hydrates $\text{BaH}^{\cdot\cdot}\text{O}^{\cdot\cdot}\cdot 9\text{H}_2\text{O}$ and $\text{SrH}^{\cdot\cdot}\text{O}^{\cdot\cdot}\cdot 9\text{H}_2\text{O}$, $24\cdot32$ and $24\cdot72$ kil.-degrees of heat are evolved; in the dissolution of the same hydrates in water, $14\cdot06$ and $15\cdot08$ kil.-degrees are absorbed.

From the values above given Berthelot infers the existence of several hydrates of potash and soda; probably contained in the solution partly in the state of dissociation.

Heat of Neutralisation of the Alkalis, Alkaline Earths, and Organic Bases (Thomsen, *J. pr. Chem.* [2], xiii. 241-270). The heats of neutralisation of the alkalis, including thallium hydrate, and of the alkaline earths, exhibit great irregularities when these bodies are dissolved as anhydrous oxides or as hydroxides; but all these anomalies disappear when the heat of neutralisation of the aqueous solutions is examined, and the resulting compounds remain in solution. In this case the quantity of heat evolved in the neutralisation of 2 equivalents of base is for hydrochloric acid $27\cdot5$ and for sulphuric acid $31\cdot3$ kil.-degrees. These values are the true heats of neutralisation of the bases mentioned. The same heat of neutralisation is exhibited by organic bases analogous in constitution to potassium hydroxide, e.g. the hydroxides of tetramethylammonium, triethylsulphine and platodiamine. The heat of neutralisation of ammonia, on the other hand, is considerably smaller; for sulphuric acid $28\cdot15$, and for hydrochloric acid $24\cdot54$; and it is not altered by the substitution of alcohol-radicles, $\text{C}^n\text{H}^{2n+1}$, for hydrogen; thus for triethylamine it is for sulphuric acid $28\cdot34$, and for hydrochloric acid $25\cdot04$. The aromatic amines, however, exhibit a much smaller heat of neutralisation; for 2 mols. aniline and toluidine, it amounts to 15 kil.-degrees for hydrochloric and 16 for sulphuric acid. Hydroxylamine also gives with hydrochloric acid only $18\cdot5$ kil.-degrees. In oxygenised organic bases the heats of neutralisation of the type is likewise lowered; thus methylquinine hydroxide gives with hydrochloric acid about 20 , whereas tetramethylammonium hydroxide gives $27\cdot5$; triethylstibine oxide gave with 1 mol. sulphuric acid only $3\cdot65$ kil.-degrees. Still greater is the difference when the oxygenated radicles are true acid radicles, as in the amides; for 1 mol. urea the heat of neutralisation is only $0\cdot13$.

Heat of Solution of Alcohols in 100-120 times their weight of Water (Berthelot, *Ann. Chim. Phys.* [5], ix. 307).

Methyl Alcohol	2	Isobutyl Alcohol	2·88
Ethyl Alcohol	2·5	Amyl Alcohol (ferment.)	2·80
Propyl Alcohol	3·05	Glycerin	1·51
Pseudopropyl Alcohol	3·45		

Heat of Solution and Neutralisation of Ethyl-sulphuric Acid (Berthelot, *Compt. rend.* lxxvii. 246).

$\text{C}^2\text{H}^4(\text{H}^{\cdot\cdot}\text{SO}^{\cdot\cdot})$ dil. + $\frac{1}{2}\text{Na}_2\text{O}$ dil.	Heat of Solution	+ 13·7
$\text{C}^2\text{H}^4(\text{H}^{\cdot\cdot}\text{SO}^{\cdot\cdot})$ „ + $\frac{1}{2}\text{BaO}$ „		+ 13·9
$\text{C}^2\text{H}^4(\text{HNaSO}^{\cdot\cdot}\cdot\text{H}_2\text{O})$ crystallised		- 3·14
$\text{C}^2\text{H}^4(\text{HNaSO}^{\cdot\cdot})$ anhyd. (dried in cold vacuum)		- 1·02
$\text{C}^2\text{H}^4(\text{HBa}^{\cdot\cdot}\text{SO}^{\cdot\cdot})\text{H}_2\text{O}$ crystallised		- 2·13
$\text{C}^2\text{H}^4(\text{HBa}^{\cdot\cdot}\text{SO}^{\cdot\cdot})$ anhyd. (dried in cold vacuum)		- 0·35

Heat of Solution of Alkaline Acetates. According to Berthelot (*Compt. rend.* lxxvii. 975) the acetates of potassium and sodium, whether dehydrated by fusion or by exposure in a vacuum at ordinary temperatures, evolve the same quantities of heat on dissolving in water, and the resulting solutions likewise exhibit the same rise of temperature when treated with hydrochloric acid. Reischauer some years ago observed that fused sodium acetate when exposed to the air takes up 14 mols. water and deliquesces to a supersaturated solution, but that the same salt when dehydrated over sulphuric acid in a vacuum takes up only 3 mols. water without essential alteration of appearance. Berthelot attributes this difference to the fact that the dehydration of the salt in a vacuum takes place very slowly, and the slightest trace of the hydrated salt enclosed in the mass will prevent the formation of a supersaturated solution, which in all probability contains chiefly the anhydrous salt.

The evolution of heat in the formation of the sodium and potassium salts of acetic and trichloroacetic acids has been determined by Longuine (*Bull. Soc. Chim.* [2], xx. 312), with the view of studying the influence of the introduction of a halogen-atom into the acid molecule. The alkali-solutions employed were of the strength of 0.75 per cent., and did not decompose the trichloroacetic acid. The quantities of heat evolved on solution were as follows:

	Kil.-degrees
Solution of Acetic acid (m. p. 16.5°; b. p. 118°) in water	0.369
„ Trichloroacetic acid „ „	2.9
Solution of Acetic acid in Caustic Potash	13.46
„ Trichloroacetic acid „	14.235
Solution of Acetic acid in Caustic Soda	13.468
„ Trichloroacetic acid „	14.166

Hence it appears that the quantities of heat evolved in the formation of these salts is determined, not only by the type and constitution of the acid, but also by the nature of the elements of which it is formed.

Thermal Changes attending the Solution and Crystallisation of Sodium Butyrate and the Allotropic modifications of Elements (Berthelot, *Compt. rend.* lxxx. 512). This salt, in the crystallised as well as in the anhydrous state, gives out heat in dissolving:

	Kil.-degrees
$\text{C}_4\text{H}_7\text{NaO}_2$, dried at 100°	+ 4.27
„ „ dried in a cold vacuum	+ 4.21
$\text{C}_4\text{H}_7\text{NaO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	+ 3.66
$\text{C}_4\text{H}_7\text{NaO}_2 \cdot 3\text{H}_2\text{O}$	+ 3.44

The formation of the crystallised hydrates from water and the anhydrous salt gives out the following quantities of heat:

$\text{C}_4\text{H}_7\text{NaO}_2 + \frac{1}{2}\text{H}_2\text{O}$ (liquid) = $\text{C}_4\text{H}_7\text{NaO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	+ 0.58
$\text{C}_4\text{H}_7\text{NaO}_2 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{5}{2}\text{H}_2\text{O}$ (liquid) = $\text{C}_4\text{H}_7\text{NaO}_2 \cdot 3\text{H}_2\text{O}$	+ 0.22

The development of heat for the first semi-molecule of water is much greater than for the other five taken together, showing that the first hydrate is not simply a mixture of the anhydrous butyrate with the highest hydrate. Deducting from these numbers the heat of fusion of water, namely 0.715 kil.-degree for each semi-molecule, the following results are obtained:

$\text{C}_4\text{H}_7\text{NaO}_2 + \frac{1}{2}\text{H}_2\text{O}$ (solid) = $\text{C}_4\text{H}_7\text{NaO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	- 0.135
$\text{C}_4\text{H}_7\text{NaO}_2 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{5}{2}\text{H}_2\text{O}$ „ = $\text{C}_4\text{H}_7\text{NaO}_2 \cdot 3\text{H}_2\text{O}$	- 3.35
$\text{C}_4\text{H}_7\text{NaO}_2 + 3\text{H}_2\text{O}$ „ = $\text{C}_4\text{H}_7\text{NaO}_2 \cdot 3\text{H}_2\text{O}$	- 3.49

The combination of solid water with solid sodium butyrate to a crystallised hydrate is therefore accompanied by a considerable absorption of heat, showing that the change of state consequent on the mere lowering of the temperature below 0°, changes the thermic sign of the combination, which, moreover, takes place directly.

Similar changes of thermic sign occur in the allotropic modifications of elements. The conversion of octohedral sulphur into solid insoluble sulphur is attended with evolution of heat, when it takes place below 18°, with no thermal change when it takes place at about 18°, and with absorption of heat above 18° to about the melting point 113°, probably also in the fluid state up to about 160°. At 160°, on the other hand, the ordinary liquid is converted into insoluble liquid sulphur, and this change is attended with evolution of heat. These changes are accompanied by unequal alteration of the specific heat of the two modifications of sulphur with the temperature. The formation and stability of the insoluble sulphur depend upon the sign of the thermal change which accompanies the reaction: at and above 160°, and below 18°, it is stable, because its formation is attended with evolution of heat; between 18°, and its melting point 113°, and probably also in the liquid state up to 160°, it undergoes spontaneous alteration attended with absorption of heat.

In consequence of the change of condition of an element with rise of temperature, a compound which at a certain temperature is unstable or explosive may become stable at a higher temperature. The formation of hydrogen selenide from its elements in their ordinary state, that is to say, from red or metallic selenium, is attended, according to Hautefeuille (*Compt. rend.* lxxvii. 1554; *Jahresh. f. Chem.* 1869, 103), with absorption of heat:



But the same combination must develop 2 units of heat if the specific heat and heat

of vaporisation of the selenium be taken into account. Hence the stability of hydrogen selenide must increase as its temperature rises; and this will account for the observation of Ditte (*2nd Suppl.* 1079) that the quantity of hydrogen selenide formed by direct combination of its elements is a function of the temperature.

Solution of Amorphous Bodies. Duvernoy (*Chem. Centr.* 1874, 428, 440) finds that the solution of bodies which have no distinct crystalline structure, but approach more or less to the amorphous state, such as gum, resins, plant-extracts, &c., is in many cases, attended with evolution of heat, or where no conspicuous change of temperature can be observed, there is, at all events, no diminution. This is shown by the following observations, in which the temperature of the solvent ranged from 15° to 20°:

Substance	Solvent	Rise of temperature
Gum Arabic	Water	1°-1.5°
Dextrin	"	1.6°
Malt Extract, dry	"	1.5°-2°
Caramel	"	1.5°
Liquorice juice	"	1.5°
Myrrh	"	1.5°-2°
Catechu	"	0.5°-0.8°
Kino	Alcohol	2.5°
Sandarac	"	1.5°-2°
Guaiac	"	1.5°-2°
Benzoin	"	1°-2°
Jalap-resin	"	1°
Shellac	"	1°
Dragon's-blood	"	1° and above
Catechu	"	0.8°-1°

Pulverised loaf-sugar or sugar-candy, dissolved in a certain quantity of distilled water, produced a fall of temperature of 2° to 3°; but when fused amorphous sugar, the so-called barley-sugar, was pulverised and dissolved in a small quantity of water at 15°, the thermometer during the dissolution rose to 18° and higher.

G. Fleury (*Compt. rend.* lxxxii. 196) observes that on mixing a solution of 60 grams of sugar in 30 g. of water with 500 g. of dilute hydrochloric acid containing 389 of hydrogen chloride, a rise of temperature from 49.5° to 52.1° takes place, which he attributes to inversion of the sugar.

Freezing Mixtures (Berthelot, *Compt. rend.* lxxviii. 1173). The three following processes take place in freezing mixtures, either singly or simultaneously. 1. Conversion of a liquid or solid body into gas (evaporation of ether or sulphur dioxide; reaction of a bicarbonate with an acid). 2. Liquefaction of a solid body by mixture with a liquid (solution of salts), or by mixture with another solid body (crystallised sulphur trioxide and snow, calcium chloride and snow, &c.) 3. Chemical reaction within a liquid, attended with the formation of substances, the solution of which absorbs more heat than that of their components (dissolved alkaline acetates and dissolved tartaric acid, according to Berthelot's experiments) or better by the formation of bodies which are decomposed by water, such as the salts of weak acids (ammonium carbonate formed by mixing an alkaline carbonate with sulphate or nitrate of ammonia), acid salts, &c.

Whichever of these three reactions may be employed, the fall of temperature $t - t_1$ may be calculated from the equation:

$$t - t_1 = \frac{Q_t}{\sum pc},$$

in which Q_t represents the heat absorbed; p, p, \dots the weights of the products; and c, c, \dots their specific heats. This temperature varies with the initial temperature t_1 , but attains its limit with the solidifying point of the mixture, on which account it is impossible to lower the temperature beyond a certain degree.

The change of temperature which takes place on mixing snow with the crystallised hydrate of sulphuric acid, $\text{SH}^2\text{O}^4.\text{H}^2\text{O}$, is the sum (algebraical) of three reactions, viz. the fusion of the hydrate and of the snow, which is attended with absorption of heat, and the combination of the two resulting liquids, which gives rise to evolution of heat:

	Kil.-degree
Fusion of $\text{SH}^2\text{O}^4.\text{H}^2\text{O}$ gives	- 3.68
" 17H ² O	- 24.31
Combination of $\text{SH}^2\text{O}^4.\text{H}^2\text{O}$ with 17H ² O	+ 9.8
	- 18.03

This is the quantity of heat absorbed for 422 grams of the mixture. To calculate therefrom the depression of temperature, this quantity of heat must be divided by the heat-capacity of the resulting mixture for a rise of temperature of 1° , that is to say, by the product of the weight and specific heat of the mixture. This gives:

$$t - t_1 = \frac{-18.03}{422 \times 0.813} = -0.0526 \text{ kilogram-degree.}$$

The degree of cold obtainable by such mixtures is greater in proportion as the components have been previously cooled to a lower temperature. The limit is determined exclusively by the solidifying point of the aqueous sulphuric acid produced, which lies extremely low. But all degrees of cold hitherto experimentally obtained with freezing mixtures fall short of the theoretical amounts, because heat is absorbed from the sides of the vessel, and the lowering of the temperature is diminished by radiation; chiefly, however, because a portion of the ice remains unmelted.

The following table of the frigorific values of various mixtures of sulphuric acid and snow has been drawn up by Pfandler (*Wien. Akad. Ber.* [2 Abth.], lxxi. 509-537), from his own observations on the evolution of heat in mixing the several hydrates of sulphuric acid with water (p. 896); the molecular heats of the hydrates of sulphuric acid; the solidifying temperature of sulphuric acid at different degrees of concentration (*ibid.* 351-391); and the latent heat of fusion of snow 79.4 , and its specific heat 0.5 determined by Bunsen:

Applicable to Mixtures of $\text{SO}_4\text{H}^2 + 2.874\text{H}^2\text{O}$ with excess of Snow. Initial Temperature of the Materials 0° .

Number of mol. snow to 1 mol. acid	Number of mol. snow dissolved at the commencement	Temperature of the resulting mixture	Final temperature of the mixture after solution of the snow	Frigorific value of the mixture per mol. for temp. τ
s	$n - 2.874$	t	τ	q
9.126	9.126	-37°	-37°	0 kil.-deg.
10.5	9.3	36	30.2	2.5
11.5	9.5	35	25	4
13	9.7	34	21.5	7
15	10	33	17.8	10
16.5	10.2	32	16.5	11
18.5	10.4	31	14.5	16
21	10.6	30	12.4	20
24	10.9	29	11	24
26.5	11.1	28	9.5	27
29.5	11.4	27	8.6	32
32.5	11.7	26	7.8	37
36	12	25	7.0	41
40	12.4	24	5.5	46
45	12.8	23	4.5	51
50	13.2	22	3.9	61
58	13.9	21	3.4	72
66	14.4	20	3.1	83
76	15.0	19	2.8	97.6
87	15.7	18	2.5	114
98	16.3	17	2.3	130
109	17.1	16	2.1	145

To cool a body down to τ , it is most advantageous to mix the hydrate $\text{SO}_4\text{H}^2 + 2.874\text{H}^2\text{O}$ with snow in such proportion that, after the snow has been melted, the mixture may have the solidifying temperature τ° . It will then, at the beginning, have a lower temperature t° . To raise the temperature from t° to τ° , a proportionally very large quantity of heat will have to be taken up by the mixture; but from τ° upwards a much smaller quantity of heat will be sufficient to raise the temperature by a given amount. Now the quantity of heat which the mixture must absorb to raise its temperature from t° to τ° is the frigorific value for the temperature τ (for 1 mol. of acid used).

Cryohydrates (F. Guthrie, *Chem. News*, xxx. 237; *Phil. Mag.* [4], xlix. 1-20, 206-218, 266-276; [5], i. 49-60; abstr. *Chem. Soc. Jour.* 1875, 333, 530; 1876, i. 336; ii. 169 1877, i. 36). Every salt soluble in water is capable of uniting with

water in definite proportion to form a solid hydrate having a distinct crystalline form, melting point and solidifying point. Those hydrates which form only at temperatures below 0° are called by Guthrie 'cryohydrates.' Thus sodium chloride unites with 10.5 (? 10) mol. water, forming a hydrate which solidifies at -23° ; ammonium chloride combines with $12\text{H}_2\text{O}$, forming a compound which solidifies at -15° .

The temperature at which a cryohydrate forms is the same as that which is produced on mixing the corresponding salt with ice, and among similar salts, that which unites with the smallest number of water-molecules to form a cryohydrate is likewise that which produces the greatest degree of cold when used to form a freezing mixture. The following table exhibits the results of experiment with several salts. The numbers in column (2) show the lowest temperature producible by mixing a salt with ice; those in (4) show the molecular proportion between the anhydrous salt and the water of the cryohydrate (water-value, aquavalent):

Formula of salt	Temperature of freezing mixture of salt and ice	Solidifying temperature of cryohydrate	Molecular ratio	Percentage of anhydrous salt	
				In the portion of cryohydrate last solidified	In the portion of cryo. solidified just before the last
(1)	(2)	(3)	(4)	(5)	(6)
NaBr	-28°	-24°	8.1	41.33	41.61
NH_4I	27	27.5	6.4	55.49	57.6
NaI	26.5	15	5.8	59.45	59.39
KI	22	22	8.5	52.07	51.72
NaCl	22	22	10.5	23.60	—
$\text{SrCl}_2 + 6\text{H}_2\text{O}$	18	17	22.9	27.57	27.5
$(\text{NH}_4)_2\text{SO}_4$	17.5	17	10.2	41.70	42.2
NH_4Br	17	17	11.1	32.12	32.17
NH_4NO_3	17	17	5.72	43.71	43.26
NaNO_3	16.5	17.5	8.13	40.80	41.3
NH_4Cl	16	15	12.1	19.27	19.27
KBr	13	13	13.94	32.15	31.80
KCl	10.5	11.4	16.61	20.03	20.07
K_2CrO_4	10.2	12	18.8	36.27	36.41
$\text{BaCl}_2 + 2\text{H}_2\text{O}$	7.2	8	37.8	23.2	24.0
$\text{Sr}(\text{NO}_3)_2$	6.0	6	33.5	25.99	25.91
$\text{MgSO}_4 + 7\text{H}_2\text{O}$	5.3	5	23.8	21.86	—
$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	5	7	20.0	30.84	—
KNO_3	3	2.6	44.6	11.20	—
Na_2CO_3	2.2	2	92.75	5.97	—
$\text{CuSO}_4 + 5\text{H}_2\text{O}$	2	2	43.7	16.89	—
$\text{FeSO}_4 + 7\text{H}_2\text{O}$	1.7	2.2	41.41	16.92	17.85
K_2SO_4	1.5	1.2	114.2	7.80	7.5
$\text{K}_2\text{Cr}_2\text{O}_7$	1	1	292.0	5.30	—
$\text{Ba}(\text{NO}_3)_2$	0.9	0.8	259.0	5.30	—
$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$	0.7	0.7	165.6	4.55	—
KClO_3	0.7	0.5	222.0	2.93	2.88
$\text{Al}(\text{NH}_4)(\text{SO}_4)_2 + 12\text{H}_2\text{O}$	0.4	0.2	261.4	4.7	4.2
HgCl_2	0.2	0.2	450.0	3.21	3.29

The solidifying point of a mixture of two salts containing the same base or the same acid, lies between those of the constituent salts; so likewise does the temperature of the mixture when used as a cryogen. When salts with different bases and acids are mixed, partial decomposition takes place, resulting in the formation of two new salts. Thus a saturated solution of a mixture of KNO_3 and Na_2SO_4 solidifies at -5° , as a mixture of NaNO_3 and K_2SO_4 , whereas NaNO_3 alone solidifies at -17° .

The following table contains the results of experiments with several mixtures of salts. The solutions were evaporated to incipient crystallisation, then cooled down till the salts appeared dry, and the temperature required for the formation of the cryohydrate was noted. The temperature of the mixture, as cryogen, in the last column, is the lowest that was observed on mixing the salt with snow or pounded ice in various proportions:

Mixed salts		Solidifying point of each constituent as cryohydrate		Temp. of final solidification of the mixture as cryohydrate	Temperature produced by the mixture as cryogen
(a.)	(b)	(a)	(b)	(a+b)	(a+b)
KNO ³	$\frac{1}{2}$ NaNO ³	2.6	-17.5	-17	-16.8 ⁺
KCl	+ NaCl	11.4	22.0	21	21.8
KCl	+ NH ⁴ Cl	11.4	15.0	17	18.0
Ba(NO ³) ²	+ Sr(NO ³) ²	0.8	6.0	4.3	5.8
BaCl ²	+ SrCl ²	8.0	17.0	8	16.7
(NH ⁴) ² SO ⁴	+ Na ² SO ⁴	17.0	0.7	7	16.0
2KNO ³	+ Na ² SO ⁴	2.6	0.7	5	---
NaNO ³	+ K ² SO ⁴	17.5	1.2	5	---
2K ² SO ⁴	+ 2NaCl	1.2	22.0	12.5	---

The following tables contain the results of experiments on the separation of Ice, or of a Hydrate, or of Anhydrous salt, from saline solutions below 0°, particular attention having been paid to prevent the supersaturation of the solution, especially with ice:

NaCl ¹ wt. p. c.	H ² O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	KNO ³ wt. p. c.	H ² O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
1	99	- 0.3°	Ice	1	99	- 0.1°	Ice
2	98	- 0.9	"	2	98	- 0.3	"
3	97	- 1.5	"	3	97	- 0.7	"
4	96	- 2.2	"	4	96	- 1.1	"
7	93	- 4.2	"	5	95	- 1.5	"
10	90	- 6.6	"	7	93	- 2.2	"
13	87	- 9.1	"	8.5	91.5	- 2.6	"
15	85	- 11.0	"	10	90	- 2.9	"
16	84	- 11.9	"	11.2	88.8	- 3.0	"
19	81	- 15.5	"	12	88.0	0.0	Cryohydrate KNO ³
20	80	- 17.0	"	13	87	+ 2.0	"
22	78	- 20.0	"	15	85	+ 6.0	"
23.6	76.4	- 22.0	Cryohydrate	20	80	+ 14.0	"
25	75	- 12.0	{ Suberyo- hydrate NaCl	25	75	+ 21.0	"
26.27	73.73	0.0		35	65	+ 35.0	"
26.5	73.5	+ 25.0	"	40	60	+ 41.0	"
28.8	73.2	+ 40.0	"				
NH ⁴ Cl wt. p. c.	H ² O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	CaCl ² wt. p. c.	H ² O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
1	99	- 0.4°	Ice	1	99	- 0.2°	Ice
3	97	- 1.6	"	2	98	- 0.5	"
5	95	- 3.1	"	3	97	- 1.1	"
7	93	- 4.6	"	4	96	- 1.6	"
10	90	- 7.1	"	5	95	- 2.1	"
13	87	- 9.9	"	7	93	- 3.3	"
15	85	- 12.0	"	10	90	- 5.5	"
16	84	- 13.0	"	15	85	- 10.5	"
17	83	- 14.0	"	20	80	- 17.5	"
18	82	- 15.0	"	28	72	- 27.5	"
19	81	- 15.8	"	36.45	73.5	- 37.0	Cryohydrate Unknown hydrate
19.27	80.73	- 16.0	Cryohydrate	39	61	0.0	CaCl ² + 6H ² O
20	80	- 15.0	NH ⁴ Cl	45	55	+ 15.5	"
22	78	- 5	"				
23.2	76.8	0	"	NaCl wt. p. c.	H ² O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
25	75	+ 8	"	1	99	- 0.7	Ice
30	70	+ 32	"	2	98	- 2.0	"

HI wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	(NH ₄) ₂ SO ₄ wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
3	97	- 3.6	Ice	10	90	- 2.6°	Ice
4	96	- 5.3	"	20	80	- 6.0	"
5	95	- 7.0	"	28.6	71.4	- 10.8	"
6	94	- 9.0	"	40	60	- 16.0	"
7	93	- 11.5	"	41.7	58.3	- 17.0	Cryohydrate (NH ₄) ₂ SO ₄
8	92	- 14.0	"	41.9	58.1	0.0	"
9	91	- 17.0	"	43.2	56.8	+ 19.0	"
10	90	- 20.5	"				
12	88	- 27.0	"				
14	86	- 35.0	"	NH ₄ NO ₃ wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
16	84	- 45.0	"				
KBr wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	10	90	- 3.5°	Ice
				20	80	- 7.0	"
				30	70	- 11.5	"
				40	60	- 17.0	"
10	90	- 3.0	Ice	43.7	56.3	- 17.2	Cryohydrate NH ₄ NO ₃
20	80	- 7.1	"	47	53	- 12.0	"
30	70	- 12.0	"	51	49	- 5.7	"
32.15	67.9	- 13.0	Cryohydrate	54.1	45.9	0.0	"
33	67	- 9.8	KBr	66.5	43.5	+ 18.1	"
34	66	- 5.0	"				
35.03	65	0	"	MgSO ₄ wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
39.7	60.3	+ 20	"				
43.2	56.8	+ 40	"				
KI wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	5	95	- 0.6°	Ice
				10	90	- 1.5	"
				15	85	- 3.0	"
				20	80	- 4.8	"
10	90	- 2.2°	Ice	21.86	78.14	- 5.0	Cryohydrate MgSO ₄ + 7H ₂ O
20	80	- 5.1	"	21.9	78.1	0.0	"
30	70	- 9.0	"	25	75	+ 15.0	"
40	60	- 14.4	"	30	70	+ 31.0	"
52.07	47.93	- 22	Cryohydrate				
55.93	44.07	0	KI	AgNO ₃ wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
58.9	41.1	+ 20	"				
61.4	38.6	+ 40	"				
NaI wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body	10	90	- 0.8°	Ice
				20	80	- 2.7	"
				30	70	- 4.7	"
				40	60	- 6.0	"
5	95	- 0.7°	Ice	48.3	51.7	- 6.5	Cryohydrate AgNO ₃
10	90	- 2.1	"	50	50	- 5.5	"
15	85	- 3.9	"	53	47	- 3.2	"
20	80	- 6.0	"	55	45	0.0	"
25	75	- 8.5	"	69.4	30.4	+ 19.5	"
30	70	- 11.8	"				
35	65	- 15.2	"	BaCl ₂ wt. p. c.	H ₂ O wt. p. c.	Temp. of formation of solid body	Constitution of solid body
40	60	- 20.5	"				
45	55	- 26.0	"				
49.2	50.8	- 30.0	Cryohydrate				
50	50	- 29.5	Suberyohydrate	5	95	- 0.9°	Ice
55	45	- 20.0	"	10	90	- 2.2	"
60	40	- 14.7	"	15	85	- 4.0	"
61.6	38.4	0.0	NaI	20	80	- 6.0	"
63.6	36.4	+ 13.0	"	21.83	78.17	- 7.5	Cryohydrate BaCl ₂ + H ₂ O
				23.98	76.02	0.0	"
				30	70	+ 25.0	"

FeSO_4 wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution	$\text{NaC}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution
5	95	- 0.2°	Ice	22	78	- 16.0	Ice
10	90	- 0.8	"	23.3	76.7	- 18.0	Cryohydrate
14.5	85.5	- 2.0	Cryohydrate	26.6	73.4	0.0	$\text{NaC}^2\text{H}_3\text{O}_2 +$? H_2O
14.9	85.1	0.0	$\text{FeSO}_4 + 7\text{H}_2\text{O}$				
NaNO_3 wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution	$\text{KC}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution
5	95	- 2.0°	Ice	5	95	- 2.0°	Ice
10	90	- 1.2	"	10	90	- 1.6	"
15	85	- 0.3	"	15	85	- 7.4	"
20	80	- 8.4	"	20	80	- 11.2	"
25	75	- 10.8	"	25	75	- 16.0	"
30	70	- 13	"	30	70	- 22.5	"
35	65	- 15.5	"				
40.8	59.2	- 17.5	Cryohydrate				
12.34	57.66	0.0	NaNO_3 or SrO Cryohydrate				
$\text{Pb}(\text{NO}_3)_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution	$\text{C}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution
5	95	- 0.3°	Ice	5	95	- 0.3°	Ice
10	90	- 0.5	"	10	90	- 0.5	"
15	85	- 0.7	"	15	85	- 0.9	"
20	80	- 1.2	"	20	80	- 1.3	"
26.23	73.77	- 2.5	Cryohydrate	25	75	- 1.8	"
29.89	70.11	0.0	$\text{Pb}(\text{NO}_3)_2$	30	70	- 2.4	"
				35	65	- 3.2	"
				40	60	- 4.1	"
				45	55	- 5.4	"
				50	50	- 7.0	"
				51.33	48.6	- 8.5	Cryohydrate
				67.4	32.67	0.0	$\text{C}^2\text{H}_3\text{O}_2$
$\text{Sr}(\text{NO}_3)_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution	$\text{C}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution
5	95	- 0.5	Ice	5	95	- 0.8°	Ice
10	90	- 1.2	"	10	90	- 2.0	"
15	85	- 2.3	"	15	85	- 3.3	"
20	80	- 3.8	"	20	80	- 5.0	"
26	74	- 6	Cryohydrate	25	75	- 6.2	"
29.62	70.38	0	$\text{Sr}(\text{NO}_3)_2$	30	70	- 8.8	"
				35	65	- 11.5	"
				40	60	- 13.9	"
				45	55	- 16.7	"
$\text{Ca}(\text{NO}_3)_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution	$\text{C}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution
5	95	- 1.1°	Ice	5	95	- 0.7°	Ice
10	90	- 2.3	"	10	90	- 1.4	"
15	85	- 4.2	"	15	85	- 2.5	"
20	80	- 6.5	"	20	80	- 3.7	"
25	75	- 9.3	"	25	75	- 4.7	"
30	70	- 12.9	"	30	70	- 6.3	"
				35	65	- 7.6	"
				40	60	- 10.1	"
				45	55	- 13.0	"
$\text{NaC}^2\text{H}_3\text{O}_2$ wt. p. c.	H_2O wt. p. c.	Temp. of formation of solid body	Constitution				
5	95	- 2.2°	Ice				
10	90	- 5.1	"				
15	85	- 9.1	"				
20	80	- 14.0	"				

Experiments on the separation of Ice from solutions of mixed salts led to the following results:

Solutions containing 20 per cent. Solid Bodies:

AgNO ₃	NH ₄ NO ₃	H ₂ O	
20 g.	10 g.	120 g.	gave ice at -4.3°
20	20	160	" 5.0
20	30	200	" 5.5
10	20	120	" 5.8

Solutions containing 30 per cent. Solid Bodies:

30 g.	15 g.	105 g.	gave ice at -6.8°
30	30	140	" 8.0
20	30	116.6	" 8.9
20	40	140	" 9.1

These values agree nearly with those calculated on the supposition that the influence of each constituent of the mixture is proportional to its mass.

In aqueous solutions of organic colloids, such as gum-arabic, white of egg, gelatin, and mixtures of the same, the separation of ice begins at 0°, and complete solidification takes place at a temperature not lower than -0.5°. No cryohydrates appear to be formed, and in the solidified masses, ice and colloid can be distinguished side by side. Consequently gum arabic, for example, is inactive as a cryogen, inasmuch as when it is mixed in the form of powder at 0° with ice, the temperature remains unaltered.

DECOMPOSITION BY HEAT—DISSOCIATION—THERMOLYSIS.

The following theory of Dissociation is proposed by A. Horstmann (*Liebigs Annalen*, clxx, 192-210). Sir William Thomson has pointed out, as a consequence of the dynamical theory of heat, that the entire universe is being gradually brought, by the sum total of natural forces, to a state in which all physical energy will be in the form of heat, and that heat so diffused that all matter will be at the same temperature (see HEAT, iii, 135). This conclusion has been put into mathematical form by Clausius (*Pogg. Ann.* cxxv, 400), who has worked out a magnitude called 'Entropy,' which, in all the changes taking place in the universe, is continually increased, but cannot be diminished by any known natural force. The limiting state above mentioned will therefore be attained when the entropy has reached its greatest possible value, and under those conditions no further changes can take place excepting those in which the entropy remains constant, as for example in the movements of the smallest particles of a body of constant temperature, in which those movements are restricted within given spaces, and their changes of velocity within fixed limits.

In dissociation-phenomena, according to Horstmann, the limiting state is brought about in a similar manner, and is attained when the entropy has become as great as it can be under the conditions of the reaction. The problem is therefore solved when we know by what circumstances and in what manner the entropy is altered during the changes under consideration. Consider, for example, the resolution of a gaseous body into gaseous constituents under a constant volume. The entropy is (1) diminished by the consumption of heat in chemical work; (2) increased by the separation from one another of the atoms of the decomposed molecules; (3) increased by the increase of distance between the still undecomposed molecules, which nevertheless must still uniformly fill the same space; (4) and (5) diminished by the increase in the number of molecules of the two products of the decomposition, and the diminution of the distances between these molecules. The entropy will therefore attain its maximum value when the greatest possible number of molecules has been decomposed, with the smallest possible expenditure of heat, and when moreover the molecules of the three gases have been moved as far apart from one another as possible. This, however, can in general happen only when the decomposition is incomplete, whence it follows that a portion of the original compound will always remain undecomposed.

Horstmann has also deduced from his theory the following conclusions, which he has verified by experiments on ammonium carbamate (*Deut. Chem. Ges. Ber.* ix, 1625):

1. The dissociation of a solid body, like chloride or carbamate of ammonium, whose constituents are all gaseous, is smaller in amount in presence of one of the products of decomposition than when the decomposition takes place in a vacuum.

2. The decrease in dissociation becomes greater as the pressure of that product of the action which remains in excess increases; the laws regulating this decrease in dissociation may be formulated mathematically.

3. The tension-decrease of each constituent of the compound is equal for the same pressure, provided that the molecule of the compound contains equal numbers of molecules of each constituent (sal-ammoniac, for instance).

4. If, on the other hand, more molecules of one constituent are present in the compound than of the other (ammonium carbamate, &c.), then the amount of influence exerted by each constituent is different from that of the others, dissociation being decreased to a greater extent by the presence of that constituent the largest number of molecules of which are present in the compound.

5. Dissociation is decreased by the same constituent in the same proportion at all temperatures, as soon as the pressure exerted by the constituent which is in excess stands to the dissociation-tension in a vacuum in the proportion corresponding with the temperature of the experiment.

The experiments on ammonium carbamate were made, without artificial heating, at temperatures between 17° and 22° , at which, according to Naumann (*2nd Suppl.* 252), the dissociation-tension of ammonium carbamate in a vacuum is between 50 and 70 mm. When the pressure of an excess of carbon dioxide amounted to about double the dissociation-tension of ammonium carbamate in a vacuum, this tension was reduced to about 40 per cent., and with a sixfold pressure of carbon dioxide at about 400 mm., it was reduced to about 20 per cent. of its original value. In presence of an excess of ammonia, the dissociation-tension had sunk to about 40 per cent. of its original value, before the pressure of the ammonia in excess amounted to three-fourths of the corresponding tension in the vacuum; with a double pressure, the tension was only 10 per cent., and with a six-fold pressure only 2 or 3 per cent. of its original value, scarcely amounting to 2 mm.

Indifferent gases, such as atmospheric air, produce no perceptible alteration in the dissociation-tension of ammonium carbamate.

On the Theory of Dissociation, see also F. Mohr (*2nd Suppl.* 636-638).

Decomposition of Phosphorus Pentachloride. The vapour-density of this compound, as determined by Dumas' method, is 3.69 (iv. 512), that is to say, about half what it should be for a condensation to 2 volumes:

$$\frac{31 + 5 \cdot 35.5}{2} \times 0.0693 = 7.2. \quad \text{This result indicates a resolution of the vapour of } \text{PCl}_5$$

by heat into PCl_3 and Cl_2 ; and in fact it appears from experiments by Wurtz (*Deut. Chem. Ges. Ber.* ii. 162; *Compt. rend.* lxxvi. 601) that when the pentachloride is volatilised at low temperatures, and the vapour mixed with air, the density of the vapour comes out nearly equal to the normal value 7.2. The numbers thus obtained were however all somewhat below this normal value, whence Wurtz infers that some amount of dissociation must have taken place, even at the comparatively low temperatures at which the experiments were conducted; and to prevent this or diminish its amount, further experiments were made in which the vapour of the pentachloride was allowed to diffuse into a space already saturated with the vapour of one of its decomposition-products, viz. the trichloride. Out of twelve determinations thus made, seven gave numbers agreeing nearly with the normal density, four approximated thereto more or less, and only one showed a sensible excess above it, probably in consequence of peculiar circumstances in the experiment. These results show that the normal vapour-density of phosphorus pentachloride is that of an undecomposed atomic compound.

On the Dissociation of Sulphur Tetrachloride, see *2nd Suppl.* 115; of Gaseous Hydrogen Iodide, p. 428 of this Supplement; of Chloral Hydrate, p. 440 of the same.

On an apparatus for exhibiting the Dissociation of Iodine Trichloride, see Brecken (*Deut. Chem. Ges. Ber.* viii. 489; *Jahresb. f. Chem.* 1875, 151).

Decomposition of Mercuric Oxide. Experiments on the decomposition by heat of pure mercuric oxide (freed from mercurous oxide by ignition with ammonium nitrate) have been made by J. Myers (*Deut. Chem. Ges. Ber.* vi. 11). The oxide was heated in a glass tube connected with a Geissler's pump, whereby the tube could be exhausted, and the pressure of the gas evolved on heating the oxide could be measured. At 150° the tension of the gas soon reaches 2 mm. of mercury, and remains constant when the heating is continued at that temperature for an hour, also when the heat is increased to 240° ; at 293° it does not exceed 2.5 mm., and at 350° it amounts to 8 mm. But above this temperature, the tension of the evolved oxygen has no superior limit, but increases continuously, though slowly, with the

duration of the experiment, amounting to 16 mm. after five hours' heating at 400° , and to 343 mm. after $7\frac{1}{4}$ hours' at 560° . Hence Myers infers that up to a certain temperature (about 350°) the dissociation of mercuric oxide by heat is normal, the number of molecules decomposed in a given time at any constant temperature being equal to the number of those which reunite by coming in contact, so that a state of equilibrium or maximum tension is attained (see Pöundler, *Pogg. Ann.* cx.xi. 54); but that above this temperature the tension has no superior limit, because the separate molecules have attained a rapidity of movement greater than that which is compatible with their recombination. The decomposition of mercuric oxide by heat exhibits the further anomaly that the tension of the liberated gas does not diminish on cooling, whether the cooling be slow or rapid.

Debray (*Compt. rend.* lxxvii. 123) objects to the conclusions drawn by Myers from the experiments above mentioned, on the ground that the vapour of mercury being constantly removed by condensation in the cooler portions of the apparatus, the conditions for the attainment of a maximum tension of decomposition did not exist, and points out that in order to study the real phenomena of decomposition, it would be necessary to heat the substance in an apparatus of uniform temperature in every part. Operating in this manner, Debray finds that when a sealed tube containing mercury and oxygen is heated to 440° , the oxygen is almost entirely absorbed, and that even on rapidly cooling the tube, the combination completes itself before a temperature can be reached at which the elements would be without action on one another. This difference of result is evidently due to the fact that in Myers's experiments the tension of the mercury vapour was very low compared with that of the oxygen. That an apparent maximum tension was obtained at temperatures below 350° was probably due to the very slow rate at which decomposition proceeds at those lower temperatures.

Decomposition of Carbonates. Joulin (*Bull. Soc. Chim.* [2], xix. 345) has examined the dissociation of metallic carbonates by heating them in a glass tube connected with a pressure-gauge and a mercurial pump. The salt was dried at a low temperature in an atmosphere of carbon dioxide, and the tube, having been exhausted, was then heated by immersing it in an oil-bath.

Manganese carbonate began to decompose at 70° . At 150° the tension of the carbon dioxide attained a certain value, 215 mm., which remained constant for that temperature; when the salt was allowed to cool, recombination took place, and the tension reverted slowly to its initial value. Above 200° the decomposition was nearly complete, and the elastic force of the gas increased constantly to two atmospheres; the carbonate became brown, and little or no reabsorption took place on cooling.

When the carbonate was heated to 100° , 150° , and 200° , then allowed to cool, and the temperature raised a second time to 100° , the extreme tension was less than one-half of the tension attained when the salt was heated for the first time to 100° , and a third heating produced no sensible alteration of the lower tension. Since no exhaustion was effected during the three operations, this result is probably due to some molecular change in the carbonate, which renders it more stable, and consequently more able to resist decomposition at low temperatures. This explanation is also strengthened by the fact that when the temperature of the bath was quickly raised, the elastic force of the gas attained a value, 489 mm., more than double of that at which it remained constant after a lengthened heating, viz. 215 mm.; a circumstance which seems to imply that the molecules are not, in the first instance, in that condition of stable equilibrium which they finally acquire when the temperature has passed a certain degree, and remained uniform for a considerable time.

The results of the experiments with silver carbonate were somewhat different from those with manganese carbonate, inasmuch as the decomposition of the carbonate and of the resulting oxide proceeded simultaneously at temperatures above 200° . Below this, the extreme tension was sensibly inferior to that of manganese carbonate under the same conditions, and the salt altogether underwent decomposition with greater facility. The decomposition was complete at 225° .

Experiments with lead carbonate (native cerussite) showed that the tension of the carbon dioxide, which at 150° was below 30 mm., rose to 75 mm. at 250° , and increased rapidly up to 300 mm.—at which complete decomposition took place—attaining in $2\frac{1}{2}$ hours a force of two atmospheres.

These experiments show that metallic carbonates are very easily decomposable, and indicate the necessity of great precautions in their preparation and drying previous to analysis.

On the Dissociation of the Acid Carbonates of Ammonium, Potassium, and Sodium in aqueous solution, see p. 409.

Decomposition of Hydrated Salts. G. Wiedemann (*J. pr. Chem.* [2], ix. 338) has examined the dissociation phenomena of several hydrated salts by introducing them into the vacuum of a barometer-tube, and measuring the depression of the mercury produced by the pressure of the evolved aqueous vapour. Before making an observation, the temperature was kept constant for about half-an-hour, in order to ensure a uniform distribution of heat through the slowly-conducting mass of the crystal. After about ten minutes, however, the level of the mercury was found to alter but very slowly. In spite of the precaution just mentioned, the results were often irregular, the tensions observed at low temperatures often differing but little from those of pure water-vapour. To obtain constant results it was necessary, before introducing the crystals into the tube, to dry them over sulphuric acid in rarefied air till they showed traces of efflorescence on the surface.

From numerous experiments on the sulphates of magnesium, zinc, cobalt, nickel, and iron (ferrous), it appears that the results obtained with any given salt, though they may differ slightly from one another at comparatively low temperatures, agree well at temperatures above 30°–35°. Moreover, the tension of the water of crystallisation is independent of the total amount of salt present, and of the space which the vapour has to fill, provided that the quantity of water which can escape from the surface of the salt is sufficient to saturate that space with vapour under the conditions of the experiment.

Hydrated salts begin to lose water at low temperatures, the vapour then showing a small degree of elasticity; as the temperature rises, the amount of water given off and the elasticity of the vapour likewise increase. Different salts exhibit different vapour-tensions at the same temperature. At 70° ferrous sulphate shows the highest vapour-tension, then follow in order the sulphates of cobalt, nickel, magnesium, and zinc. At temperatures above the melting points of these salts the tensions of their vapours increase with rise of temperature faster than below their melting points, but no sudden increase occurs at the melting point.

If p and P be the elasticities of the vapours of pure water and of crystalline water respectively, and if the densities of these vapours vary at every temperature as the elasticities; if also G be the weight of a given volume (1 cubic meter) of saturated water-vapour at the temperature t , and g be the weight of an equal volume of vapour from the crystals, then—

$$g = G \cdot \frac{p}{P}$$

in the following table the values of G and g are calculated in grams:—

	Water	Magnesium sulphate	Zinc sulphate	Ferrous sulphate	Cobalt sulphate	Nickel sulphate
t	G	g	g	g	g	g
25	22.7	18.0	14.5	15.6	17.2	11.3
30	30.1	25.3	19.1	19.9	22.9	25.3
35	39.3	33.0	28.2	28.1	33.2	33.0
40	50.9	43.6	40.3	37.1	43.6	43.6
45	65.3	54.9	52.4	50.3	56.7	57.2
50	82.9	59.5	56.8	58.1	61.4	63.1
55	104.6	88.1	80.1	90.1	93.9	92.1
60	130.6	107.5	100.9	114.1	117.1	115.0
65	162.0	130.0	121.7	140.8	145.6	143.0
70	199.4	160.0	145.4	175.9	177.1	175.3
75	243.7	195.1	(186.6)	222.1	213.2	211.0
80	295.9	229.8	(230.3)	267.9	255.4	252.2

To calculate the amounts by weight of crystallised salt which must give up its water in order to fill 1 cubic meter with vapour (supposing the salt to be completely dehydrated), the values of g must be multiplied by the numbers 1.97, 2.29, 2.22, 2.24 and 2.24 respectively.

A. Naumann (*Deut. Chem. Ges. Ber.* vii. 1573–1583) is of opinion that Wiedemann's conclusions, as also those of Debray (*1st Suppl.* 425), with respect to the tension of the vapours emitted in the decomposition of hydrated salts, are incorrect, probably because the observations at each particular temperature were not continued long enough. The main result of his own observations is that *the vapour-tension actually exhibited by a hydrated salt during decomposition at any particular temperature is not constant*. On theoretical grounds, indeed, a hydrated salt of constant and uniform

composition throughout might be expected to give off at any fixed temperature a vapour of constant tension. Practically, however, this perfect uniformity of composition in the salt cannot be preserved or even attained, because the water given off on heating is continually being reabsorbed by the dehydrated portions of the salt, whence arises a continual alteration in the condition of the salt, and consequently in the tension of the vapour given off from it.

These changes in the state of a hydrated salt under the influence of heat are well seen in the case of cupric sulphate, on account of the change of colour consequent on the dehydration. A crystal of this salt placed in the vacuum of Hofmann's vapour-density apparatus (*1st Suppl.* 1127), and exposed to the temperature of boiling alcohol, turns white, if of sufficient size compared with the vacuum-space, on particular spots, especially where it touches the glass or the mercury, these parts being heated sooner than the rest. As the tension gradually increases, these white spots extend, and others appear on previously unattacked parts of the surface. But even after an hour's heating the tension still goes on increasing, though very slowly, whilst the white of the portions first attacked, passes through dirty-white to greenish-white, and at the same time the crystal is attacked to a greater depth. Sometimes particular faces of the crystal remain quite blue, and if the experiment be repeated after previous slow cooling, whereby the attacked parts are restored to their blue colour—just those faces which had previously remained unattacked are the first to exhibit the white spots. The darkening of the previously attacked portions from reabsorption of water, while the vapour-tension goes on increasing, shows that partially dehydrated cupric sulphate has a lower vapour-tension than the fully hydrated salt, and that no equilibrium of tension can be attained, till, by partial dehydration of still undecomposed portions of the crystal and reabsorption of water by the first and most completely dehydrated portions, the entire crystal has attained a uniform composition, for which the salt will require to be kept at the same temperature for weeks or perhaps even for months. If the crystal is proportionately small, but still of a size considerably greater than is required to saturate the available space with water-vapour at the given temperature, its whole surface is very quickly attacked, but gradually becomes darker again as the vapour-tension increases. After an hour's heating, the increase of the tension becomes so slow as to lead to the idea that a state of equilibrium is about to be established. That this however is not the case might be shown by careful observation of the tension at a temperature kept constant for a considerable time (which however would be difficult), or by a slight lowering of the temperature, which would be found to produce, not a decrease, but after some time an increase of the vapour-tension, showing that at the previously existing higher temperature the state of equilibrium had not been attained.

The vapour-tensions attained after equal times in different experiments made at the same temperature do not agree, and they are likewise different when the experiment is repeated with the same quantity of the salt. The greatest alteration of form and structure takes place when the water is reabsorbed after cooling. On repeating the experiment at the same temperature, a vapour-tension equal to that previously observed is first attained, but more quickly, and afterwards a higher tension. If the cooling be so conducted that the water cannot be precipitated in the upper part of the vacuum, and then be taken up again by the crystal, with formation of numerous elevations and depressions, but may be enclosed between the surface of the tube and the rising mercury, and thereby prevented from acting on the crystal, the latter undergoes less alteration and exhibits more equal vapour-tensions on repeated heating. Even at the ordinary temperature of a room, transparent crystals, well defined all round, and with sharp edges and smooth faces, exhibited a lower tension than those which were less well-defined or had fracture-surfaces. In certain series of experiments also, on cooling down from a higher to the ordinary temperature, the vapour-tension never returned to the lower amount exhibited by a crystal which had never been raised above the ordinary temperature and thereby essentially altered in structure and composition (Naumann). On the other hand, Wiedemann (*Pogg. Ann.* cliii. 612) maintains that cupric sulphate belongs to that class of hydrates in which the influence of the air adhering to the crystals, and of the water enclosed in them, is such as to render it almost impossible to obtain concordant results in any experiments made to determine their vapour-tensions.

Precht a. Krant (*Liebig's Annalen*, clxxviii. 129-149) are of opinion that in the experiments of Delray (*1st Suppl.* 425), and in those of Wiedemann and Naumann above noticed, sufficient attention has not been paid to two circumstances which have great influence on the course of the dissociation, viz. the quantity of the salt present, and the magnitude of the space to be filled by the vapour.* From their own experi-

* According to Wiedemann, these conditions have no influence on the result, provided the salt present contains sufficient water to saturate the space with vapour (p. 1012).

ments, made with a modified form of Hofmann's vapour-density apparatus, on *gypsum*, *cadmium sulphate*, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, *ferrous sulphate*, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, *ammonio-ferrous sulphate*, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, *ammonia-alum* and *potash-alum*, they conclude that, at a given temperature in a limited vacuum, the vapour-tension of a hydrated salt is a function of its quantity, increasing with the quantity, and approximating to a limit which would probably be reached only when the quantity of the salt was infinite. If, on the other hand, the temperature and the quantity of the salt are fixed, the attainable tension will be determined by the extent of the vacuum space, a small vacuum determining a comparatively high, and a large vacuum a comparatively low tension. Silicates, such as diopase, $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$, chrysocolla, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, and okenite, $\text{Ca}_2\text{SiO}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$, give off their water only at temperatures which are too high to allow of observations in a vacuum. These silicates, heated in a stream of dry air, began, for the most part, to give off their water at 100° , but the loss did not in any case amount to 1 mol. or even to a simple fraction thereof; at 300° more water was given off, but in no case was it possible to recognise distinct differences, from which it would be inferred that these silicates contained water in different modes of combination.

The decomposition of hydrates by heat has also been studied by J. B. Hannay (*Chem. Soc. Jour.* 1877, ii. 381-395) and by W. Ramsay (*ibid.* 395-399). Hannay has determined the loss of weight which various hydrates sustain in successive equal intervals of time when they are heated to different temperatures in a current of air. In general a hydrate parts with its water more or less quickly up to a certain point, after which the rate of dehydration becomes suddenly less and continues uniform up to another definite point, and so on. These sudden alterations in the rate of dehydration point to the formation of lower hydrates, which give off their water less quickly. Thus *magnesian sulphate*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, lost at 100° in four minutes 8.36 p. water, whereby it was reduced to $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$. The dehydration went on at a nearly uniform but slower rate, till about 29 or 30 p. water had gone off in forty-five minutes, leaving the trihydrate, $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$. The weight then diminished more slowly till the dihydrate, $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$, was left, after which it became extremely slow, till the remaining salt had the composition $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Similar results were obtained with *sodium sulphate*, *zinc sulphate*, *calcium chloride*, and *strontium chloride*.*

Ramsay has made similar experiments on the amorphous hydrates of alumina and ferric oxide, from which it appears that the variation in the rate of dehydration of hydrated alumina from $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ downwards is perfectly continuous, the curve which represents it not exhibiting any sudden break at the points corresponding with $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The same also is the case with the hydrates of ferric oxide, with the exception of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, at which there is a sudden break of continuity in the rate of dehydration. Hence Ramsay infers that, if there are really four or five definite hydrates of alumina or ferric oxide, their vapour-tensions must differ but very slightly one from the other; and he regards it as probable either that the hydrates $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, &c. do not exist as definite compounds (except $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), or else that there are a great number of hydrates of alumina and of ferric oxide, whose vapour-tensions differ from one another but very slightly, so that the smallest rise or fall of temperature is sufficient to convert a higher into a lower hydrate, and the contrary. *Lead oxide*, on the other hand, forms two definite hydrates, $3\text{PbO} \cdot \text{H}_2\text{O}$ and $2\text{PbO} \cdot \text{H}_2\text{O}$.

The vapour-tensions occurring in the dissociation of salts containing water of crystallisation have been investigated by A. H. Pureau (*Ann. Phys. Chem.* [2], i. 39-63) in the case of $\text{SrCl}_2 + 6\text{H}_2\text{O}$, $\text{CuSO}_4 + 5\text{H}_2\text{O}$, $\text{U}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$, and $\text{BaCl}_2 + 2\text{H}_2\text{O}$. In the investigations relating to this subject described in the preceding pages and in 1st *Suppl.* 425, the state of decomposition of a compound was modified by the introduction of different quantities of the substance into a vacuum. Pureau, on the other hand, examines the tension of dissociation by introducing into the vacuum a constant quantity of a crystalline powder in different states of dehydration. For this purpose the vapour is pumped out by a method similar to that which was applied to the carbon dioxide in Delray's experiments on calc spar (1st *Suppl.* 425). Up to 60° , the mode of variation of the tensions of salts containing water of crystallisation is the same as that for pure water, the curves all running parallel to Regnault's tension-curve for aqueous vapour. Moreover, the tension of dissociation is not a function of the state of decomposition of the salt. It is true that when the water is gradually withdrawn from the salt, the tension alters at a certain temperature, but this alteration is sudden. It is possible, therefore, that the salts investigated may exist in different states of equilibrium with their water of crystallisation. The results of these experiments are

* The papers above referred to contain numerous tables, and diagrams of curves, showing the rates of decomposition of the several salts at different temperatures.

at variance with Pfandler's theory, and with the mathematical developments of Horstmann (p. 1009). Finally, Parreau draws attention to the following facts: The curves deduced from his observations follow one another according to the number of molecules of crystallisation-water, whereas Wiedemann's curves, which all relate to salts with $7H_2O$, cut one another and lie close together. The tensions of strontium chloride and uranium sulphate agree together when both salts contain only $\frac{1}{2}$ mol. water; and those of copper sulphate and uranium sulphate agree when both salts contain 3 mol. water. These results might find their explanation in the somewhat bold hypothesis that the dissociation-tensions of salts containing water of crystallisation depend only on the temperature and on the number of molecules of crystallisation water, and are independent of the nature of the salt.

• *Decomposition of Crystallised Potash-alum.*—A. Naumann (*Deut. Chem. Ges. Ber.* x. 456) finds that this salt, when heated to 100° in a sealed tube, gradually decomposes after fusion, its water of crystallisation being separated, and a solid body being deposited, probably consisting of the anhydrous alum; and at the same time there is formed in the liquid, with the aid of the water set free, a basic compound of alumina, potash, sulphuric acid, and water, analogous to that which, according to former observations of Naumann, is produced in aqueous solutions of alum heated to 100° (see p. 66 of this Supplement). The decomposition of alum in closed vessels takes place also to a small amount even at 78° , at which temperature the crystallised alum still retains its form, but not at 34° .

On the Dissociation of Chrome-alum in Aqueous Solution, see p. 68.

Decomposition of Ammoniacal Salts in Aqueous Solution at low Temperatures.—A. R. Leeds (*Sill. Am. J.* [3], vii. 197) has examined the circumstances of these decompositions, by observing the reaction of the vapour emitted from the solution at various temperatures, mostly between 17° and 20° . The reagent employed was alizarin-paper, which, in contact with an alkali or with a solution in which an alkaline reaction is developed, immediately changes from yellow to red. The following are the results:—

Salts	Parts in 100°	Reaction of Liquid	Temperature	Reaction of Vapour
Ammonium Chloride	10.60	slightly acid	37°	strongly alkaline
	5.30	"	38.5	alkaline
	2.65	"	39.3	slightly alkaline
	1.325	"	39.2	"
Ammonium Sulphate	45.62	acid	50.5	alkaline
	22.81	"	51	slightly alkaline
	11.40	"	50.5	"
Ammonium Oxalate	saturated at 75°	strongly alkaline	— 1	strongly alkaline
Ammonium Acetate	saturated at 17°	acid	55	alkaline

The point of sensible dissociation doubtless depends on the circumstances of the experiment, and on the delicacy of the apparatus and reagents employed. The temperatures above given must therefore be regarded, not as absolute, but as relative and valuable only as indicative of the comparative dissociability of these salts in aqueous solution.

Decomposition of Calcium Chloride in Aqueous Solution.—A boiling solution of this salt begins to give off hydrochloric acid, as indicated by the acid reaction of the condensed vapours, when its boiling point rises to 148° , indicating a degree of concentration corresponding with the formula, $CaCl_2 + 4H_2O$. When the solution is distilled in a retort, the acid reaction does not show itself till the boiling point rises to 160° , evidently because the portions of hydrochloric acid first given off dissolve in the water which condenses on the upper part of the retort, and are carried back with it into the liquid (Dibbitts, *Archives néerlandaises*, viii. 295).

RADIANT HEAT.

Diathermancy. 1. Of Rock Salt. From experiments by H. Buff (*Pogg. Ann.* clviii. 177–213), it appears that rock salt absorbs a considerable portion of the heat which falls upon it. The complete diathermancy attributed to it by Melloni is

only apparent, the fact being that rock salt absorbs only the heat rays that are absorbed by atmospheric air. Now in Melloni's experiments the heat which fell upon the rock salt had already traversed a stratum of air, so that it no longer contained any rays that could be absorbed by the salt. See also J. B. Harrison (*Phil. Mag.* [5], iii. 424).

2. *Of Metals and Paper.*—Aymonnet (*Compt. rend.* lxxxiv. 259) concludes from experiments on the diathermancy of these bodies, viewed in connection with the observations of Wiedemann & Franz (v. 71) on the rapidity with which the equilibrium of temperature is restored in bars: (1). That metals and paper are not athermanous. (2). That they are more diathermanous for the dark heat-rays emitted from metallic bodies below 100° than for luminous heat-rays, or those which are emitted just below redness. (3). That their absorbing power is less than that of water. (4). That it is possible to discover a mathematical relation between the absorbing power of a body and its conducting power.

On the Reflection of Heat from Metals, see Knoblauch (*Ann. Phys. Chem.* [2], i. 1-13).

3. *Of Vapours.* The absorbing powers of the following vapours for heat from different sources have been investigated by G. L. Hoorweg (*Pogg. Ann.* clv. 385-402).

Leslie's Cube	Absorption	Heated Copper plate coated with Lamp-black	Absorption	Hot Brick	Absorption
Water-vapour	1.7	Water-vapour	2	Water-vapour	2.3
Carbon Disulphide	2.1	Carbon Disulphide	5	Carbon Disulphide	—
Alcohol	17	Ethyl Sulphide	19.7	Alcohol	26
Methyl Alcohol	18	Alcohol	21	Ethyl Sulphide	27.5
Ethyl Sulphide	18	Methyl Alcohol	23	Ethyl Formate	28.6
Ethyl Formate	22.1	Ethyl Formate	23.2	Ethyl Acetate	32.6
Ethyl Acetate	26.5	Ethyl Acetate	27	Methyl Alcohol	37
Total (emitted)	100	Total (emitted)	100	Total (emitted)	100

Hoorweg's experiments likewise show that in vapours—as long known with respect to solids and liquids—each successive stratum transmits a larger proportion of rays than the preceding.

Influence of Length of the Ascending Air-current.

	9 cm.	Air-column of: 50 cm.	100 cm.
Water-vapour	imperceptible	1.6	2
Alcohol „	9	17	21

The disagreement between the results of Tyndall and of Magnus with regard to the absorption of heat-rays by moist air is attributed by Hoorweg to the fact that Tyndall overestimated the amount of absorption, in consequence of neglecting or underestimating that which was due to the vapour condensed on the glass plates with which his tube was closed, while Magnus, on the contrary, underestimated it in consequence of using too short a tube.

According to H. Buff (*Pogg. Ann.* clviii. 177) the diathermancy of hydrogen gas is very nearly equal to that of a vacuum. Dry air absorbs from 50 to 60 per cent. of the heat-rays, which penetrate it from a source of heat raised to the boiling point of water. The absorptive power of moist air exceeds that of dry air by several units per cent., but not nearly to the extent maintained by some physicists.

4. *Absorptive power of Elementary Bodies in Solution.*—From observations on the absorption of heat-rays by solutions, Aymonnet infers (*Compt. rend.* lxxxiii. 97) that the heat-absorbing power of all the elementary bodies referred to their atomic weights is the same, provided (1) that they are dissolved in the same liquid; (2) that they are constituents of bodies of analogous chemical constitution.

5. *Influence of Temperature on Absorptive Power.*—According to Aymonnet (*Compt. rend.* lxxxii. 153), reduction of temperature diminishes the diathermancy of flint glass, but increases that of a solution of iodine in chloroform.

6. *Distribution of Heat in the Spectrum of the Electric Light.*—By experiments with a battery of 50-100 large Bunsen's elements, Desains finds that when the rays of the electric lamp are passed through a column of water 3 to 4 cm. long, the heat-intensity of the dark part of the spectrum is considerably diminished, while the heat of the luminous part remains nearly unaltered, amounting, as in the solar spectrum (1st Suppl. 689), to about a third of the total quantity in the spectrum. The electric spectrum in fact agrees nearly with the solar spectrum in all respects, excepting that it is somewhat less extended, especially towards the violet end (*Compt. rend.* lxxxiv. 285).

CONDUCTION OF HEAT.

1. **In Solids.** *Isothermal surfaces in Crystals* (v. 73).—Sénarmont's method of determining the isothermal surfaces of crystals, which consists in coating a thin slice of the crystal with wax, heating the surface strongly at one point, and measuring the ellipse formed round this point by the melting wax (*Ann. Chim. Phys.* [3], xxi. 457), has been modified by W. C. Röntgen (*Pogg. Ann.* cli. 603) as follows: A well-cleaned plate of the crystal, e.g. a plate of quartz cut parallel to the axis, is breathed upon rather strongly in such a manner that the moisture may cover it in a thin uniform film, not in drops. If now a pointed metal rod strongly heated in a flame be set perpendicularly on the centre of the plate, the film of moisture will evaporate round the point in a well-defined ellipse. The experiment may be interrupted when the figure has attained any desired dimensions, and the figure fixed by quickly strewing lycopodium on the surface, and tapping cautiously on the plate so as to make the lycopodium stick only on those parts from which the moisture has not been evaporated. The elliptic figure thus left is so sharply defined that its dimensions may be measured with great exactness. In two square plates of quartz cut parallel to the axis, the ratio of the elliptic axes was found by this method to vary between the numbers 1.274 and 1.323.

C. Pappe (*Ann. Phys. Chem.* [2], i. 126–147) has examined, by a modification of Sénarmont's method, the form of the isothermal surfaces in triclinic cupric sulphate. The mean values of the axes of the isothermal surface, regarded as an ellipsoid, were found to be $a : b : c = 0.939 : 0.860 : 1$; a being coincident with the crystallographic axis A , and the other two being situated in the plane of the two crystallographic axes B and C , and forming with them the angle $16^\circ 27'$, the axis b lying between $+B$ and $+C$.

According to Jannettaz (*Compt. rend.* lxxv. 1501) the axis of greatest heat-conduction in uniaxial crystals is parallel to the direction of easiest cleavage; if the crystal exhibits several directions of cleavage, the axis of easiest conduction is parallel to the direction of the greater of the two projections, one parallel and the other perpendicular to the principal axis.

For tourmaline, apatite, and pyromorphite, this rule is undecided, on account of the indistinctness of their cleavage; calcspar and emerald form exceptions to it; and these two minerals further show the peculiarity of contracting when heated, the one in the direction normal to the axis, the other parallel to it. The rule applies also to biaxial crystals, in which in fact it was first noticed by Jannettaz.

In rocks, e.g. granite, gneiss, tale-slate, mica-slate, and serpentine, heat is conducted with the greatest facility along those surfaces, planes, and lines between which there is the smallest amount of cohesion (Jannettaz, *Compt. rend.* lxxviii. 1202; *Jahresh. f. Chem.* 1874, 73).

In Soils. A. v. Littrow (*Wien. Akad. Ber.* [2 Abth.], lxxi. 99–151) has compared the heat-conductivities of different soils by placing the bulbs of thermometers at distances of 6, 12, 12 and 24 cm. from a source of heat, in a caoutchouc cylinder filled with the soil. In the case of dry soils the readings were taken at intervals of ten minutes; with wet ones every hour. The results obtained were (1). The mechanical condition of the soil exerts the greatest influence on its conducting power; the finer the state of division the less being the conductivity of the soil. Presence of organic matter considerably lessens the conducting power. (2). The petrographical and chemical composition of the soil is of small importance compared with its mechanical condition, but lime and magnesia seem to lower the conductivity. (3). All kinds of soil conduct heat better when wet than when dry, since the air in their pores is replaced by the better conductor—water. (4). The conducting power of wet soil is greater than that of water, from which it follows (5) that the materials which form the soil are in themselves better conductors than water. (6). The conducting power of dry soils lies between that of water and that of air, while the conducting power of wet soils is greater than that of water; so that the conductivity of water is between the two.

In Metals. From the experiments of Decharme (*Compt. rend.* lxxxii. 731, 815), the rate at which heat travels along a bar of iron is, at any point, inversely proportional to the square of the distance of that point from the source of heat. According to Naccari a. Bellati (*Cimento* [3], i. 72, 107), the heat-conductivity of iron is not affected by magnetisation.

According to Herwig (*Pogg. Ann.* cii. 177) the heat-conductivity of mercury between the temperatures of 40° and 160° is perfectly constant.

In Ebonite. J. Stefan (*Wien. Akad. Ber.* [2 Abth.], lxxiv. 438–462), from experiments on the heat-conductivity of ebonite, has calculated the quotient k obtained

by dividing this magnitude by the specific heat referred to the unit of volume, one series of experiments giving $k = 0.00928$, and another series $k = 0.00938$, these numbers having reference to the centimeter as the unit of length, and the second as the unit of time. On the magnitude k depends the rapidity with which differences of temperature in the interior of a body become equalised, and therefore also the rapidity with which a body cools down when exposed to a uniform temperature all round, as when it is immersed in ice. As this property of bodies is seldom noticed, Stefan has given the values of k for several substances, in order to show the place of ebonite among them :

Hydrogen gas	$k = 1.81$	
Copper	0.81	
Air	0.26	
Iron	0.18	
Ice	0.011	
Glass	0.0034	
Water	0.0015	
Ebonite	0.00093	

From k , the heat-conducting power K is calculated by the formula $K = kcs$, in which c is the specific heat and s the specific gravity of the body. For ebonite, Stefan found $c = 0.23$, $s = 1.22$; therefore $cs = 0.2806$, and $K = 0.00026$. According to their heat-conducting powers, therefore, the eight bodies above mentioned range themselves in the following order :

Copper	$K = 1$
Iron	0.17
Ice	0.0057
Glass	0.0016
Water	0.0015
Hydrogen gas	0.00039
Ebonite	0.00026
Air	0.000055

On the conducting powers of different kinds of glass for heat and for electricity, see ELECTRICITY (p. 722).

Heat-conduction in Liquids. The order of conductivity of a few liquids for heat and electricity, was determined in 1868 by Paalzow (*Pogg. Ann.* cxxxiv. 613) with the results shown in the following table, the best conductors in each column being placed first :

Conducting power for :

<i>Heat.</i>	<i>Electricity.</i>
Mercury.	Mercury.
Water.	Sulphuric acid (sp. gr. 1.25).
Cupric Sulphate (conc.)	Sodium Chloride
Sulphuric acid (sp. gr. 1.25).	Zinc Sulphate
Zinc Sulphate (conc.)	Cupric Sulphate
Sodium Chloride (conc.)	Water.

Experiments on the relative heat-conductivities of a considerable number of liquids were made about the same time by F. Guthrie, from which he concluded that of all known liquids (except mercury) water is the best conductor of heat, and certain others, *e.g.* ethylene bromide, amyl iodide, and ethyl iodide the worst (see 1st *Suppl.* 692).

Absolute values of the heat-conducting powers of water and a few other liquids have been obtained by Lundquist (*Pogg. Ann.* cliii. 481), whose results confirm the statement of Paalzow that the conducting powers of liquids for heat and electricity are not proportional to one another, and that the conducting power of liquids for heat varies much less than their conducting powers for electricity.

The following table exhibits the heat-conductivities of certain liquids referred to the centimeter and second as units of length and time, calculated by A. Winkelmann (*Pogg. Ann.* cliii. 481-498) from observations on the rate of cooling of the liquids enclosed in cylindrical vessels. The specific gravities and specific heats are also given :

	Heat-conductivity	Spec. gravity	Spec. heat
Water	0·001540	1	1
Sodium Chloride solution, 33·33 per cent.	0·002675	1·187	0·773
Potassium Chloride solution, 20 per cent.	0·001912	1·110	0·808
Alcohol	0·001506	0·795	0·690
Carbon Disulphide	0·002003	1·268	0·259
Glycerin	0·000748	1·220	0·612

According to E. Sacher (*Dingl. pol. J.* cccxiv. 343) the conduction of heat in liquids whose density decreases from below upwards takes place very slowly in the downward direction. The experiments were made by carefully pouring five layers of alcohol, sp. gr. 0·98 to 0·82, one upon the other. The same result was obtained by cooling experiments.

Heat-conduction in Gases. The following values are given by A. Winkelmann (*Pogg. Ann.* clvii. 497 555 and cliv. 177–191):

	Experiment	Theory
Air	1	1
Carbon Dioxide	0·60	0·86
Ethylene	0·79	1·13
Methane	1·23	1·76
Nitrogen Dioxide	0·88	0·96
Nitrogen Monoxide	0·69	0·91

Also the proportions of the heat-conductivity of hydrogen to those of the following gases (each taken as unity) at 7·5°:

Water-vapour	8·88
Alcohol-vapour	11·07
CS ₂ -vapour	18·08
Ammonia	6·93
Ether-vapour	11·22

The alteration of conducting power with the temperature is expressed by the ratio of the heat-conductivity of a gas at τ to that at 0°, namely, by $(1 + \bar{\gamma}\tau) : 1$. The observations gave the following values of the temperature-coefficients $\bar{\gamma}$, on the assumption of a constant specific heat for mercury, or $\bar{\gamma}$, on the supposition that the specific heat of mercury decreases with rise of temperature. The coefficients $\bar{\gamma}$ correspond with the value 0·00277, which was found for air and hydrogen:

	$\bar{\gamma}$	$\bar{\gamma}$
Ethylene	0·006110	0·005751
Nitrogen Monoxide	4468	4149
Water-vapour	4712	4388
Alcohol-vapour	6517	6117
CS ₂ -vapour	6078	5717
Ammonia	5475	5128
Ether-vapour	7400	7012
Carbon Dioxide	5300	4970

On the Mechanical Theory of Heat, see THERMODYNAMICS.

HEBRONITE. This name is proposed by v. Kobell (*J. pr. Chem.* [2], vii. 45), instead of *Montebrasite*, for the hydrated aluminium fluophosphate occurring at Montebras (Creuse), and at Hebron in the State of Maine (U. S.) (*2nd Suppl.* 972). A specimen of hebronite from Auburn in Maine gave by analysis:

P ₂ O ₅	Al ₂ O ₃	Li	Na	F	H ₂ O	Sp. gr.
49·00	37·00	3·44	0·79	5·50	4·50 = 100·23	3·06

HELECODEA. On the microscopic appearances and behaviour with reagents of the fibres of *Helecodea* or *Billbergia Leopoldii*, and certain other plants of the Bromeliaceous order, see p. 349 of this Supplement.

HELENIN. This substance, obtained from the root of elecampane (*Inula Hellenum*), and hitherto regarded, on the authority of Gerhardt, as a distinct bitter principle, C₂₁H₃₂O₃ (iii. 138), appears from the experiments of J. Kaller (*Deut. Chem. Ges. Ber.* vi. 1506) to be a mixture of two different substances. In fact, when helenin (m. p. 72°), prepared according to Gerhardt's directions, is heated to 50° or 60° in a current of air, a body melting at 61° sublimes, and the melting point of the residue rises above 72°; the former of these substances (inula-camphor) likewise passes over when Gerhardt's helenin is distilled with water.

To obtain pure helenin, the root is exhausted with hot alcohol, and the needle-shaped crystals thereby obtained, which at first melt at 72° , are repeatedly crystallised till their melting point rises to 109° – 110° . Helenin thus purified forms colourless inodorous needles, having a faint taste, nearly insoluble in water, easily soluble in alcohol, and having a composition represented by the empirical formula $C^{10}H^{16}O$. All attempts to determine the molecular formula by the preparation of bromo-, nitro-derivatives, &c., were unsuccessful.

Isula-camphor, the second constituent of crude helenin, remains in the alcoholic mother-liquors, and is difficult to obtain in the pure state. A preparation not quite pure gave, on distillation with phosphorus pentasulphide, a hydrocarbon (Gerhardt's *helenene*) having the formula of cymene, $C^{10}H^{14}$. Isula-camphor, probably $C^{10}H^{16}O$, may be obtained pure, though only in small quantity, by distilling elecampane-root with water, as above mentioned; when thus prepared, it forms prismatic needles having an odour like that of peppermint, and a burning aromatic taste.

HELIANTHUS. The chemical composition of the sunflower (*Helianthus annuus*) has been examined by G. C. Wittstein (*Arch. Pharm.* [3], viii. 289). The plant deprived of its seed loses on drying 72.25 per cent. water; the dry residue yields 1.9 per cent. ash; the air-dried seed 4.173 per cent. ash. Different sorts of the seed contain from 41 to 60 per cent. husk, and 40 to 50 per cent. kernel; the kernels yield, by extraction, from 40 to 50.5 per cent. of a fatty oil. The ash of the plant and of its seed have the following composition: *a.* Plant; *b.* Seed.

	K	Na	K ₂ O	Na ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	Cl	SO ₃	P ₂ O ₅	SiO ₂	CO ₂
<i>a.</i>	3.68	1.09	44.01	—	9.85	5.29	9.28	0.17	5.00	1.34	0.97	0.69	21.63 = 100
<i>b.</i>	—	1.40	14.48	4.71	6.81	10.96	0.23	1.43	2.16	2.09	31.85	10.81	13.07 = 100

The involucre of the sunflower (grown in Algeria) contains, according to M. Chardon (*Pharm. J. Trans.* [3], iv. 322), a transparent, colourless, resinous mass smelling like the resin of *Pinus maritima*, soluble in alcohol, and drying up, when exposed to the air in thin layers, to a hard brittle mass. This substance does not reduce Fehling's solution at the boiling heat; when slowly heated, it gives off a volatile oil, and leaves a residue resembling colophony.

HEMIALBUMIN. See PROTEIDS.

HEMIPINIC ACID, $C^{10}H^{10}O^6 = C^6H^7(OCH^3)^2(CO^2H)^2$, *Dimethyl-phthalic acid*. See NARCOTINE-DERIVATIVES.

HEMIPROTEIN. See PROTEIDS.

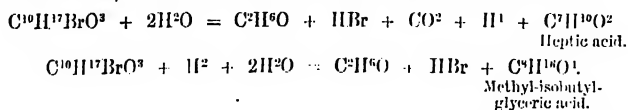
HENWOODITE. A mineral occurring in blue or bluish-green radiate spherules on the pyrolusite of the West Phoenix Mine, Cornwall. Streak white, with a bluish-green tinge. Sp. gr. 2.67. Composition:

Al ₂ O ₃	P ₂ O ₅	SiO ₂	CaO	CaO	Fe ₂ O ₃	H ₂ O	Loss
18.24	48.94	1.37	0.54	7.10	2.74	17.10	3.97 = 100

(J. H. Collins, *Jahrb. f. Min.* 1876, 411).

HEPTANE, C^7H^{16} . See PARAFFINS.

HEPTIC ACID, $C^{12}H^{22}O^7 = 3C^2H^{10}O^2.H^2O$ (Demargay, *Compt. rend.* lxxxvi. 1135). An acid, formed, together with methyl-isobutylglyceric acid, $C^4H^{10}O^4 = C^2H(CH^3)(CH^3)O^4$, and other products, by the action of alcoholic potash on ethylic bromoisobutylacetacetate, $C^{10}H^{17}BrO^3 = CH^3.CO.CBr(C^2H^5).COOC^2H^5$:



To prepare these compounds, isobutylacetylacetic ether, mixed with its own weight of ice, is treated with successive small portions of bromine, care being taken that the temperature does not rise above -5° . When all the bromine has been added, the liquid is allowed to get warm, and soon becomes colourless; it is then poured in small portions into excess of strong alcoholic potash. From the liquid free from alcohol, hydrochloric acid separates an oil which, when purified and fractionally distilled, yields isocaproic (isobutylacetic) acid (see HEXOIC ACID), whilst isobutylmethylglyceric acid remains in the flask in the form of a mobile liquid, changed for the most part by heating into gummy anhydrides, a small portion, however, distilling with the aqueous vapour.

Heptic, oxyheptic, and glycolic acids may be extracted by ether from the water from which the preceding acids have been distilled, and are separated by crystallisation from water and chloroform, in which heptic acid alone is soluble. Heptic acid forms flat needles, having a satiny lustre, and melting at 151° to a colourless liquid, which boils and decomposes at a higher temperature. It is slightly soluble in cold water, colours ferric chloride pale brown, and decomposes carbonates only on heating. Its composition is represented by the formula $3C^7H^{10}O^2 + H^2O$, and that of its barium salt by $C^7H^{10}BaO^7$; it would seem, therefore, that the acid should have the formula $C^7H^{12}O^7$. Closer examination shows, however, that it is only in its less energetic reactions that the triple molecule forms a single group, whilst bromine, phosphorus pentachloride, &c. break up this group.

The study of oxyheptic acid, $C^7H^{10}O^3$, confirms this view of the composition of heptic acid. This body is easily formed by the action of alcoholic potash on ethylic dibromisobutylmethylglycerate. After crystallisation from boiling water, it forms pearly scales, melting at 185° , and having the composition $3C^7H^{10}O^3.H^2O$. Pentachloride of phosphorus converts it into a chloride, $C^7H^8OCl^5$, boiling, with decomposition, at 21° . Ammonia converts this chloride into the corresponding amide, melting and decomposing at 251° . Alcohol converts the chloride into the ether $C^7H^{10}O^2.OC^2H^5$, boiling at 129° – 130° , under a pressure of 10 c.m.; at 230° – 240° , with decomposition, under ordinary pressure. If ammonia be added to the solution of the chloride in a large quantity of alcohol, another amide, $C^7H^{10}O^2.NH^2$, is obtained on evaporation, in slender needles melting at 87° .

HEPTINE, $C^7H^{12} = CH^3.CH^2.CH^2.CH^2.CH^2.C \equiv CH$ (also, but incorrectly, named *Heptylidene*, and *Enanthylidene*). A hydrocarbon, homologous with acetylene or ethine, C^2H^2 ; discovered by Lamprecht, who obtained it by the action of sodium on monochlorheptylene, $C^7H^{13}Cl$, and, together with heptylene, by the action of sodium ethylate or alcoholic potash on heptylene chloride, $C^7H^{11}Cl^2$ (iii. 148); afterwards more fully examined by Rubien (*1st Suppl.* 696). Bnylants (*Ber.* viii. 406) prepares it by the action of potassium hydroxide on the chloride or bromide, $C^7H^{11}Cl^2$ or $C^7H^{11}Br^2$, obtained by treating enanthaldehyde with PCl^5 or PBr^5 . It boils at 100° – 110° , and reacts with ammoniacal copper and silver solutions like acetylene.

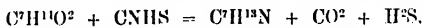
When the bromide $C^7H^{11}Br^2$ is used for the preparation, a *bromheptylene*, $C^7H^{13}Br$, is obtained as a bye-product, in the form of a colourless pungent liquid boiling at 165° .

HEPTOIC ACIDS, $C^7H^{14}O^2 = C^6H^{13}.COOH$. The properties of normal heptoic or enanthylic acid, $CH^3.(CH^2)^5.COOH$, prepared by oxidation of enanthol with nitric or chromic acid, and by oxidation of normal heptyl alcohol from heptane, have been described by Grimshaw & Schorlemmer (*2nd Suppl.* 869). The same acid has been more recently studied by Mehlig (*Liebigs Annalen*, clxxxv. 358–372), who prepares it by oxidising enanthal with nitric acid, and by Lieben & Janacek (*ibid.* clxxvii. 126–152), who obtain it by saponification of the cyanide $C^6H^{13}.CN$, prepared from normal hexyl alcohol.

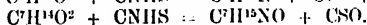
Ammonium heptoate is easily soluble in water, alcohol, and ether, and non-crystalline. The *normal potassium salt*, $C^7H^{13}KO^2$, was obtained by Mehlig as a white silky non-crystalline mass; by Grimshaw & Schorlemmer as a transparent jelly. The *sodium salt*, $C^7H^{13}NaO^2$, separates in needles or as a jelly, according to the rate of cooling (G. and S.) The *zinc, lead, and copper salts* have been already described (*2nd Suppl.* 870).

The following derivatives of normal heptoic or enanthylic acid are also described by Mehlig (*loc. cit.*)

Enanthonitril, or *Heptyl Cyanide*, $C^7H^{13}N = C^6H^{13}.CN$, is formed, together with enanthamide, by heating enanthylic acid with potassium thiocyanate (Letts's reaction):



and



Other reactions, however, go on at the same time, by which the yield of these products is greatly reduced.

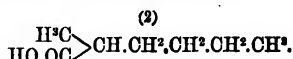
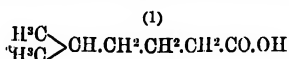
Enanthonitril is a clear, colourless, neutral liquid, insoluble in water but soluble in alcohol and ether. It boils at 175° – 178° . Sp. gr. = 0.895 at 22° . It is decomposed by boiling with potash, yielding potassium enanthylate and ammonia. It quickly alters when exposed to the air.

Enanthamide, $C^7H^{13}NO = C^6H^{13}O.NH^2$, is formed simultaneously with the nitril; also by the action of ammonia on enanthylic anhydride. When pure, it is easily soluble in water, alcohol, and ether. It crystallises from water in iridescent laminae

and from alcohol in pointed needles melting at 94°–95°. By boiling with water or with alkalis it is resolved into enanthylic acid and ammonia.

Enanthylic anhydride, $(C^7H^{13}O)^2O$, obtained by distilling the acid with phosphorus pentachloride and heating the resulting enanthylic chloride with potassium enanthylate, is a thick colourless liquid having a neutral reaction, and boiling at 268°–271° without decomposition. Sp. gr. 0.932 at 21°. Reacts with ammonia to form the amide.

Isoheptic Acid is produced by oxidation of isoheptyl alcohol (p. 1025), and may therefore be constituted according to either of the following formulæ:



The isoprimary alcohol obtained by Grimshaw from othyl-amyl (2nd Suppl. 642) yielded by oxidation an acid which boiled at 210°–213°; and the isoheptyl alcohol which Schorlemmer obtained from diethyldimethylmethane yielded by oxidation an acid boiling at 209°–213°. The barium, calcium, and silver salts of these two acids also closely resembled one another in their properties (see table on next page). It is possible, however, that one of the acids in question may be constituted according to the first, and the other according to the second of the formulæ above given.

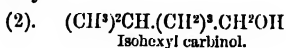
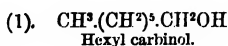
Diethyl-methylacetic Acid, $C(C^2H^5)^2(CH^3) \cdot CO \cdot H$, has been examined by E. Idanow (*Bull. Soc. Chim.* [2], xxvi. 450), who prepares it by acting on zinc-ethyl with acetyl chloride, converting the resulting diethyl-methyl-carbinyl iodide into the corresponding iodide; heating this compound for six to eight days with potassium cyanide; and digesting the crude diethyl-methyl-carbinyl cyanide at 120°–140° with fuming hydrochloric acid. The product thus obtained is distilled, mixed with caustic soda, and evaporated to dryness; the residue is treated with alcohol, which dissolves out the organic salt; and this, when decomposed by sulphuric acid, yields the free diethyl-methylacetic acid in the form of a colourless-oily liquid nearly insoluble in water, and having a faint, not unpleasant odour. After drying over dehydrated sodium sulphate and phosphoric anhydride, it boils at 207°–208°, and does not solidify at –20°. Its normal potassium salt, $(C^2H^5)^2(CH^3)C \cdot CO^2K$, is very soluble and non-crystalline; the acid salt, $C^2H^5K O^2 \cdot C^2H^5O^2$, separates on cooling in stellate groups of needles. The lead salt is a white precipitate, slightly soluble in cold water, the solution becoming turbid when heated.

The following table (p. 1023) exhibits a comparative view of the properties of normal heptic acid prepared in the several ways above mentioned, also of isoheptic acid and diethyl-dimethylacetic acid.

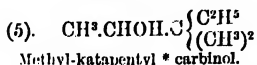
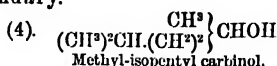
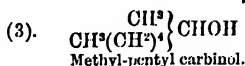
HEPTOIC ALDEHYDE, $C^7H^{14}O$ or $C^6H^{13} \cdot CHO$. *Enanthaldehyde*, *Enanthal*, *Enanthol*.—A polymeric of this aldehyde is formed by prolonged contact with potassium carbonate. It is a solid body which may be purified by recrystallisation, melts at 51°–52°, and when heated to 160°–170°, yields a liquid distillate which easily solidifies on cooling, but previous to that change of state, exhibits the characteristic reactions of an aldehyde with alkaline bisulphites and with silver nitrate. Similar polymeric modifications are formed in like manner with acetaldehyde and benzaldehyde (Braylants, *Ber.* viii. 414).

HEPTYL ALCOHOLS, $C^7H^{16}O$. Eleven alcohols of this group are at present known, two primary, four secondary, and five tertiary, viz.

Primary.



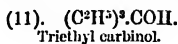
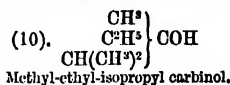
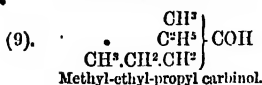
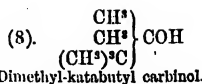
Secondary.



* The prefix *kata* is applied to the radicals of tertiary alcohols.

Normal Heptoic Acid			Isoheptoic Acid			Diethyl-methylacetic Acid	
	(Grimshaw & Schorlemmer)	From Chuanthal (Nehlis)	From Heptane (Grimshaw & Schorlemmer)	From Normal Heptyl Cyanide (Lichten u. Junczek)	From Ethyl-amyl (Grimshaw)	From Dimethyl-diethyl-methane (Schorlemmer)	Idanow
Free Acid	Boils under 763 mm. pressure at 223°-234°. Melts and solidifies at -10°-5°. Sp. gr. (at 0° = 0.9345; at 85° = 0.9278; at 10° = 0.9208; at 29° = 0.9110; at 40° = 1)	Boils at 210°. Solidifies at -12° to a crystalline mass which melts at -5°. Sp. gr. at 21° = 0.916	Did not solidify in a freezing mixture (probably from admixture of impurities) (at 0° = 0.9359; at 9° = 0.9349; at 28° = 0.9235)	Boils under 734 mm. at 234°. Solidifies in a freezing mixture to a crystalline mass melting at -10°. Sp. gr. (at 0° = 0.935; at 20° = 0.9198; at 40° = 0.9084)	Boils at 210°-213°. Colourless only liquid having a sour and unpleasant odour	Boils at 209°-213°	Boils at 207°-208°
Ethyl Ether	Boils under 763 mm. at 187°-189°. Remains liquid at -20°. Sp. gr. at 16° = 0.8735	Distill at 189°-188°. Remains liquid at -14°. Sp. gr. at 21° = 0.871		Boils under 747.6 mm. at 189.3°. Sp. gr. 0.8679 at 0°, 0.8716 at 20°, 0.8589 at 40°			
Barium Salt	(C ¹⁷ H ³³ O ²) ₂ Ba. Thin laminae or broad needles. 100 c.c. of the aqueous solution saturated at 12° contain 1.7 grm. of the salt.	White iridescent laminae, melting with decomposition at 238°-239°. Dissolves in 64 pts. water at 22°; moderately soluble in boiling 85 per cent. alcohol	Thin laminae or broad needles. 100 c.c. of the solution saturated at 12° contain 1.774 grams of this salt		Remains as an amorphous pellicle when its solution is left to evaporate	Amorphous	+5H ² O. Separates on rapid cooling in small groups of fine needles; on slow cooling in flat prisms. Gives off all its water over 50°H ² . Not easily wetted by water but dissolves freely therein. forming supersaturated solutions
Calcium Salt	(C ¹⁷ H ³³ O ²) ₂ Ca. Thin flat needles. 100 c.c. of the solution saturated at 8.5° contain 0.9046 grm. of the anhydrous salt		Thin flat needles. 100 c.c. of the solution saturated at 8.5° contain 0.9046 grm. of the anhydrous salt	+H ² O. 100 c.c. of the solution saturated at 11°-13° contain 0.9165 c. 0.9268 grm. of the anhydrous salt	Crystallises by evaporation at a gentle heat in small needles	Separates on evaporation by heat as an amorphous film; but crystallises by spontaneous evaporation in long transparent needles or prisms	
Silver Salt	Small woolly needles	White bulky precipitate turned brown by light. Insoluble in cold water and alcohol; slightly soluble in boiling water			Separates from hot solution as a granular or flocculent precipitate. Crystallises by spontaneous evaporation in small needles	Flocculent crystalline precipitate	Dulky white precipitate, slightly soluble in boiling water, and separating on cooling in tufts of small needles, turned brown by light

Tertiary.



PRIMARY HEPTYL ALCOHOLS.

(1). **Normal Heptyl Alcohol**, or **Hexyl Carbinol**, is produced: *a.* From cœnanthaldehyde by the action of sodium-amalgam. The best way of proceeding is to dissolve the aldehyde in strong acetic acid, add liquid sodium-amalgam to the solution, saponify the resulting heptyl acetate with potash, and rectify the alcohol over sodium. Heptyl alcohol thus prepared boils at 175.5° under a pressure of 755 mm. (Schorlemmer, *Liebig's Annalen*, clxxvii. 304 *); see also *2nd Suppl.* 644.

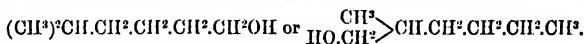
C. J. Cross (*Chem. Soc. J.* 1877, ii. 123) also finds that normal heptyl alcohol prepared from cœnanthaldehyde boils at 175.5° (bar. 764 mm.), and has a specific gravity of 0.838 at 0°, 0.830 at 16°, 0.821 at 27°. The *chloride*, $\text{C}^7\text{H}_{15}\text{Cl}$, prepared from it by the action of hydrochloric acid, boils at 159.2° (bar. 750 mm.), and has a specific gravity 0.881 at 16°. The *bromide*, $\text{C}^7\text{H}_{15}\text{Br}$, boils at 178.5° (bar. 750.6 mm.), and has a specific gravity of 1.133 at 16°. The *iodide*, $\text{C}^7\text{H}_{15}\text{I}$, boils at 201° (bar. 754.8 mm.), and has the specific gravity 1.346 at 16°.

The *acetate*, $\text{C}^7\text{H}_{15}.\text{C}^2\text{H}_3\text{O}_2$, prepared by heating the iodide at 180° with potassium acetate and glacial acetic acid, has a fragrant odour of pears, boils at 191.5° (bar. 758.5), and has the specific gravity 0.874 at 16°.

Heptyl cœnanthylate, $\text{C}^7\text{H}_{15}.\text{C}^7\text{H}_{13}\text{O}_2$, prepared by heating the iodide at 180° with silver cœnanthylate (normal), is a liquid having a faint but disagreeable fatty odour, and boiling at 270°–275° (bar. 760 mm.)

Heptyl-ethyl oxide, $\text{C}^7\text{H}_{15}.\text{O}.\text{C}^2\text{H}_5$, produced by heating the iodide with an alcoholic solution of sodium ethylate, is a liquid having an odour of lemons, boiling at 166° (bar. 755 mm.), and having a specific gravity of 0.791 at 0°; 0.790 at 16° (Cross).

(2). **Isoheptyl Alcohol**, or **Isohexyl Carbinol**, either



This alcohol is obtained, together with methyl-isopentyl carbinol, by passing dry chlorine into the vapour of boiling ethyl-amy, converting the resulting mixture of primary and secondary chlorides into acetates, and saponifying the latter. The iso-primary alcohol boils at about 165° (Grimshaw, *2nd Suppl.* 642).

SECONDARY HEPTYL ALCOHOLS.

(3). **Methyl-pentyl Carbinol**, $\text{CH}^3.\text{CHOH}.\text{CH}^2.\text{CH}^3$ (T. M. Morgan, *Chem. Soc. J.* 1875, 301). This alcohol has been obtained from normal heptane (from Pennsylvanian petroleum) by the following process. The hydrocarbon (b. p. 96°–99°), treated with chlorine in the manner above described, yielded a mixture of chlorides boiling between 144° and 156°, which, when passed in the state of vapour over quicklime heated to a temperature just short of redness, were converted into heptylenes, C^7H_{14} , boiling between 96° and 99°. On mixing these heptylenes with strong hydrochloric acid, and passing a stream of hydrogen chloride through the mixture, a heptyl chloride was formed, which boiled with decomposition between 138° and 142°, and was resolved by heating with potassium acetate and acetic acid into hydrogen chloride and a heptylene. This latter treated with hydriodic acid was converted into an iodide, from which, by decomposition with lead acetate and saponification of the resulting acetic ether, a heptyl alcohol was obtained, which boiled between 140° and

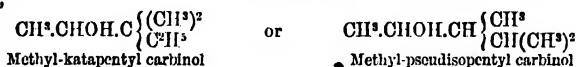
* The boiling point of the alcohol is there misprinted 155.5°.

141°, and was converted by oxidation with chromic acid mixture, first into a ketone (b. p. 137°–141°), and afterwards into a mixture of acetic and normal butyric acids; it appears therefore to be a secondary alcohol, but its constitution has not been exactly determined.

The portion of the heptylenes not attacked by cold hydrochloric acid, yielded, when heated to 120° with hydriodic acid, an iodide, partly convertible by the action of lead acetate at 120° into a heptyl acetate boiling between 170° and 174°, and yielding by saponification a heptyl alcohol boiling between 156° and 158°. This alcohol, oxidised by cold chromic acid solution, yielded a ketone boiling between 146° and 149°, and convertible by further oxidation into a mixture of acetic and normal valeric acids. Hence, according to Popoff's law (1st Suppl. 765), the ketone consists of methyl-pentyl ketone, and the alcohol of methyl-pentyl carbinol.

(4). **Methyl-isopentyl Carbinol**, or **Methyl-amyl Carbinol**, $\text{CH}^3\cdot\text{CHOH}\cdot(\text{CH}^3)_2\cdot\text{CH}(\text{CH}^3)_2$, is obtained, together with the isoprimary alcohol, from ethyl-amyl or dimethyl-butyl-methane, in the manner already mentioned (p. 1024). Boils at 146°–148°. Converted by oxidation into methyl-amyl ketone, $\text{CH}^3\cdot\text{CO}\cdot\text{C}^6\text{H}^{11}$ (Grimshaw).

(5). A third secondary heptyl alcohol, which may be represented by either of the formulæ,



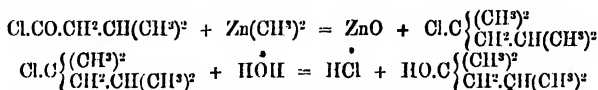
most probably by the former, is obtained in like manner from dimethyl-diethyl-methane, $\text{C}(\text{CH}^3)_2(\text{C}^2\text{H}^5)_2$. It boils at 148°–150° (Schorlemmer, *Chem. Soc. J.* 1873, 320; see also 2nd Suppl. 643).

(6). **Di-isopropyl Carbinol**, $(\text{CH}^3)_2\text{CH}\cdot\text{CHOH}\cdot\text{CH}(\text{CH}^3)_2$, obtained by the action of nascent hydrogen on di-isopropyl ketone, is a liquid having a pleasant ethereal odour like that of peppermint, a specific gravity 0.8323 at 17°, and boiling at 130°–132°. It dissolves partially in water, easily in alcohol and ether. By gradual oxidation with chromic acid solution, it is reconverted into di-isopropyl ketone (R. Munch, *Ber.* vii. 1129).

TERTIARY HEPTYL ALCOHOLS.

(7). **Dimethyl-isobutyl Carbinol**, $\frac{\text{H}^3\text{C}}{\text{H}^3\text{C}}\text{>COH}\cdot\text{CH}^2\cdot\text{CH}\left\{\begin{matrix}\text{CH}^3 \\ \text{CH}^3\end{matrix}\right\}$. Discovered by Markownikoff (*Zeitschr. f. Chem.* 1871, 268), and further examined by Pawlow (*Liebigs Annalen*, clxxiii. 192). Markownikoff prepares it from the pseudoheptylene, $(\text{CH}^3)_2=\text{C}=\text{CH}-\text{CH}=(\text{CH}^3)_2$, obtained by heating oxyisocaprylic acid with water (p. 1027). On passing gaseous hydrogen iodide through this hydrocarbon, dimethyl-isobutyl iodide, $(\text{CH}^3)_2=\text{C}=\text{CH}-\text{CH}_2-\text{CH}=(\text{CH}^3)_2$, is obtained as a heavy liquid, which, when treated with moist silver oxide, yields the tertiary alcohol (Markownikoff).

Pawlow obtains the same alcohol by dropping valeryl chloride (1 mol.) into cooled zinc-methyl (2 mols.), leaving the mixture to itself for 30 days, and then decomposing it with water:



The product is fractionated by distillation, and treated with acid sodium sulphite to remove admixed methyl-isobutyl ketone.

Dimethyl-isobutyl carbinol is a colourless liquid, lighter than water, nearly insoluble therein, and has a camphorous odour. When oxidised with chromic acid mixture, it is converted, according to Pawlow, into acetic and isobutyric acids; according to Markownikoff, it is resolved thereby into water and pseudoheptylene.

Dimethyl-isobutyl-carbinyl Iodide, $(\text{CH}^3)_2\cdot\text{Cl}\cdot\text{CH}^2\cdot\text{CH}(\text{CH}^3)_2$, formed from the alcohol by saturation with hydriodic acid, with addition of a little water, or from the pseudoheptylene by direct combination, is a heavy oil which is decomposed by distillation, and converted by heating with alcoholic potash into a heptylene which differs in constitution from that just mentioned, and is reconverted by silver oxide and water into dimethyl-isobutyl carbinol (Pawlow). The corresponding *bromide*, $\text{C}^7\text{H}^{13}\text{Br}$, formed also from pseudoheptylene by direct combination, is converted by heating with water at 100°, chiefly into pseudoheptylene, together with a small quantity of dimethyl-isobutyl carbinol.

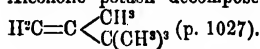
(8). **Dimethyl-katabutyl Carbinol**, $\text{HO.C}\left\{\begin{smallmatrix} (\text{CH}^3)^2 \\ \text{C}(\text{CH}^3)_2 \end{smallmatrix}\right.$, *Pentamethyl-ethol*, c. *Pentamethylated Ethyl Alcohol*, $\text{C}(\text{CH}^3)_2\text{—C}(\text{CH}^3)_2\text{OH}$ (Butlerow, *Liebigs Annalen*, clxxvii. 176).—This alcohol is formed by the action of trimethylacetyl chloride, $\text{C}(\text{CH}^3)_2\text{COCl}$, (1 mol.) on zinc-methyl (2 mols.) A few lumps of sodium are thrown into the freshly-prepared mixture; the liquid decanted from the zinc thereby separated is heated for some hours at $60^\circ\text{--}65^\circ$ in a sealed tube; the contents, which have become crystalline, are then decomposed with water, whereupon marsh gas is given off; the mass is acidulated with hydrochloric acid; and the oil which then separates is distilled with water. By repeating these operations several times, pressing the crystals which separate, and drying them over caustic baryta, the dimethyl-katabutyl carbinol is obtained as a hydrate having the composition $2\text{C}^7\text{H}^{14}\text{O} + \text{H}^2\text{O}$. This hydrate forms long prismatic needles, slightly soluble in water, easily in alcohol and ether, has a burning taste, and a camphorous and at the same time mouldy smell. It begins to boil and give off water at 100° , and at 130° the anhydrous alcohol begins to distil. The dehydration may be also partially effected by leaving the hydrate over baryta in a closed vessel, and if this operation is performed at a temperature of 100° , the dehydration becomes complete in a few days, the anhydrous alcohol remaining as an oil.

Warm and dilute chromic acid mixture acts very slowly on the hydrate, but bromine acts readily on it, yielding a white solid, which by the further action of bromine is converted into an oily body. The solid product appears to be a mixture of $\text{C}^7\text{H}^{13}\text{Br}$ and $\text{C}^7\text{H}^{11}\text{Br}^2$.

Pentamethyl Ethol, prepared from its hydrate, as above described, forms an oil which boils at 131° . When strongly cooled, it solidifies, forming white needles which melt at $+17^\circ$; and it readily absorbs water, reproducing the hydrate, so that when moist air is passed into the upper part of a bottle containing the alcohol, glistening leaflets of the hydrate are produced, and float about in the air over the liquid.

Pentamethyl-ethyl chloride, $\text{C}^7\text{H}^{13}\text{Cl}$, or $\text{C}^2(\text{CH}^3)_2\text{Cl}$, obtained by treating the hydrate with phosphorus pentachloride, and washing the product, is a white solid, smelling like 'artificial camphor.' It separates from its alcoholic solution in white needles, which melt at 136° , and sublime rapidly at a higher temperature; but it is also volatile at the ordinary temperature, and yields up its chlorine to a warm solution of silver nitrate.

The *iodide* prepared by the action of hydriodic acid on the alcohol, smells like the chloride, is soluble in alcohol, and melts with partial decomposition at $140^\circ\text{--}142^\circ$. Alcoholic potash decomposes it, forming a heptylene which has the constitution



(9 and 10). **Methyl-ethyl-propyl Carbinol**, $\text{HO.C}\left\{\begin{smallmatrix} \text{CH}^3 \\ \text{C}^2\text{H}^5 \\ \text{CH}^2\text{CH}^2\text{CH}^3 \end{smallmatrix}\right.$, and

Methyl-ethyl-isopropyl Carbinol, $\text{HO.C}\left\{\begin{smallmatrix} \text{CH}^3 \\ \text{C}^2\text{H}^5 \\ \text{CH}(\text{CH}^3)_2 \end{smallmatrix}\right.$, are formed by the action

of a mixture of zinc-methyl and zinc-ethyl on the chlorides of butyryl and isobutyryl respectively. The former boils at $135^\circ\text{--}138^\circ$; the heptylene prepared from its iodide at $90^\circ\text{--}95^\circ$; the latter alcohol boils at $124^\circ\text{--}127^\circ$, its heptylene at $75^\circ\text{--}80^\circ$ (Pawlow, *Liebigs Annalen*, clxxxviii. 122).

(11). **Triethyl-carbinol**, $(\text{C}^2\text{H}^5)_3\text{COH}$. This alcohol, already described (2nd Suppl. 1182), is formed by the action of zinc-ethyl on propionyl chloride. It is a colourless liquid, having a specific gravity of 0.8593 at 0° , becoming viscid at 20° , and boiling at $140^\circ\text{--}142^\circ$ (Nahapetian).

HEPTYLENES, C^7H^{14} . These hydrocarbons are obtained, together with heptyl acetates, by heating the several heptyl chlorides with potassium acetate and glacial acetic acid. 1. The mixture of heptylenes thus obtained from the chlorides produced by the action of chlorine on normal heptane, boils at $98^\circ\text{--}99^\circ$ (Schorlemmer, *Chem. Soc. J.* 1873, 322); between 96° and 99° (Morgan, *ibid.* 1875, 303). Respecting the reaction of these heptylenes with hydrochloric acid, see p. 1025.

The heptylene which boils at 96° unites with water, forming a hydrate which when dropped into a vessel heated over an oil-bath is resolved into water, a resin, and a body which boils at 140° , and exhibits the properties of an unsaturated alcohol (Le Bel, *Compt. rend.* lxxxi. 967).

2. The heptylene from ethyl-amyl boils at 91° and has a sp. gr. of 0.7060 at 16°

(Grimshaw, *Chem. Soc. J.* 1873, 313); that from dimethyl-diethyl-methane boils at 90°-92° (Schorlemmer, *Chem. Soc. J.* 1873, 320).

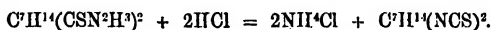
3. A heptylene having the constitution $\text{CH}(\text{CH}^3)^2 \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH}^3 \\ \text{CH}_2 \end{smallmatrix}$ is produced by the action of alcoholic potash at 100° on dimethyl-isobutyl-carbinyl iodide (p. 1026). It is a liquid boiling at 83°-84°, has a sp. gr. of 0.7144 at 0°, and unites directly with bromine to form a dibromide. It also unites with hydriodic acid, reproducing dimethyl-isobutyl-carbinyl iodide, $\text{C}^6\text{H}^{13}\text{I}$ (Pawlow, p. 1026).

4. A heptylene having the constitution $(\text{CH}^3)^2\text{C}=\text{CH}-\text{CH}(\text{CH}^3)^2$ is produced by heating oxyisocaprolic acid (2nd Suppl. 885) with water; $\text{C}^6\text{H}^{10}\text{O}^3 = \text{C}^7\text{H}^{14} + \text{CO}^2 + \text{H}^2\text{O}$. It boils at 81°-83°; has a sp. gr. of 0.6985 at 14°; is readily acted on by bromine, with evolution of HBr , and unites with HI , producing methyl-isobutyl-carbinyl iodide (Markownikoff, *Zeitsch. f. Chem.* 1871, 268).

5. A heptylene, $\text{H}^2\text{C}=\text{C} \begin{smallmatrix} \text{CH}^3 \\ \text{C}(\text{CH}^3)^2 \end{smallmatrix}$, which may be called *methyl-katabutyl-ethylene*, is formed by the action of alcoholic potash on dimethyl-katabutyl iodide (p. 1026). It is a liquid which does not solidify in a freezing mixture, and forms a solid, translucent, very volatile dibromide (Butlerow).

6. The heptylene obtained from methyl-ethyl-propyl carbinol boils at 90°-95°; that from methyl-ethyl-isopropyl carbinol boils at 75°-80° (Pawlow).

HEPTYLENE-THIOCARBIMIDE, $\text{C}^7\text{H}^{14}(\text{NCS})^2$. When thiocarbamide and amantol are dissolved together in alcohol, a few drops of hydrochloric acid then added, and the mixture warmed, *ananthodisulphureide*, $\text{C}^7\text{H}^{14}(\text{CSN}^2\text{H}^3)^2$, is formed; and this, on addition of a few more drops of hydrochloric acid, is converted into heptyleno-thiocarbimide:



Heptyleno-thiocarbimide is a thick oily liquid having a very repulsive odour. Alcoholic ammonia converts it into the disulphureide (H. Schiff, *Ber.* xi. 830).

HERACLEUM. The essential oil of the cow-parsnep (*Heracleum sphondylium*) has been examined by W. Möslinger (*Liebig's Annalen*, clxxxv. 26). 126 kilos. of the fruits gathered in 1874 yielded, by distillation with steam, 1163 grams of oil (0.92 per cent.); 173.16 kilos. gathered in the autumn of 1875 yielded 1460.5 grams of oil (0.84 per cent.), the yield in each case being affected by the mode of distillation, and being most abundant when the distillation was conducted in a current of steam, and not merely from a vessel filled with water.

The examination of the oil yielded results differing in some respects from those obtained by Zincke (1st Suppl. 697; 2nd Suppl. 644), whose statements indeed are inapplicable to oil obtained from fruits either not quite ripe or only lately ripened, and appear to be true, if at all, only for fruits which have been quite ripe for a long time. The oil of *Heracleum sphondylium* agrees perfectly in composition, so far as regards its lowest boiling portions, with that of *Heracleum giganteum*; both these oils contain ethyl butyrate. The distillation-water contains chiefly—together with ammonia, but no substituted ammonias—methyl alcohol, ethyl alcohol (in smaller quantity), acetic acid and caproic acid, but no perceptible quantity of butyric acid. The oil contains also small quantities of hexyl compounds, apparently only the acetate; that of *H. giganteum* contains chiefly hexyl butyrate (2nd Suppl. 644). The oil of *H. sphondylium* does not contain octyl butyrate, but the octyl-ethers of higher fatty acids, viz. caproic, cupric, and lauric; whether it contains also those of the intermediate acids, or of acids still higher in the series, is not yet determined.

The oil of 1874 yielded, after several rectifications, the following fractions:

Boiling Point . . .	110°-175°	175°-190°	190°-200°	200°-203°
Weight of Fraction . .	6.5	15.75	4.5	32 grams
Boiling Point . . .	203°-206°	206°-208°	208°-210°	210°-240°
Weight of Fraction . .	702.75	104.5	35.25	117.5 grams
Boiling Point . . .	240°-291°	Residue with crystals		
Weight of Fraction . .	42.5	28 grams		

Fraction 110°-175° consists chiefly of ethyl butyrate; it has an acid reaction, due to free acetic and butyric acids. Fraction 203°-206° consists of octyl acetate; 210°-240° of octyl acetate and caproate. Free octyl alcohol, observed by Zincke, was not found by Möslinger. Hexyl alcohol was found in the fruit gathered in 1875. The lowest fraction of the oil (80°-110°) yielded by saponification a liquid containing hexyl and octyl alcohols.

HERAPATHITE. See CINCHONA ALKALOIDS (p. 490).

HERNIARIA. The ash of *Herniaria glabra*, grown on siliceous and on dolomitic soil, has been analysed by G. G. Wittstein (*Arch. Pharm.* [3], iv. 341).

1. From siliceous soil. Total ash in air-dried plant, 7.132 per cent.

K ² O	Na ² O	Na(with Cl)	CaO	MgO	Al ² O ³	Fe ² O ³
24.380	4.110	1.702	14.349	6.300	1.321	1.038
Mn ² O ³	Cl	SO ³	PO ³	SiO ²	CO ²	
—	2.624	1.717	9.729	14.445	17.694.	

2. From dolomitic soil. Total ash, 6.622 per cent.

K ² O	Na ² O	Na(with Cl)	CaO	MgO	Al ² O ³	Fe ² O ³
8.680	3.860	6.691	30.400	14.839	1.755	0.130
Mn ² O ³	Cl	SO ³	PO ³	SiO ²	CO ²	
—	1.066	1.746	8.421	6.367	21.505.	

HESPERETIC ACID, and **HESPERETIN**. See the next Article.

HESPERIDENE, C¹⁰H¹⁶. A terpene contained in the volatile oil of orange-peel. It boils at 178° (corr.); is oxidised by *chromic acid mixture*, chiefly to carbonic acid and water, together with acetic acid, a trace of formic acid, and a small quantity of a liquid compound, C¹⁰H¹⁶O, isomeric with camphor; no toluic or terephthalic acid is formed. With *nitric acid*, it yields oxalic acid, and an acid called hesperic acid, which, when dried over sulphuric acid, has the composition C¹⁰H¹⁶O¹⁷.2H²O; no terephthalic acid is formed in the reaction. Hesperidene is not converted into a more highly hydrogenised compound by heating with hydriodic acid and phosphorus. When *hydriodic acid gas* is passed into it, a liquid hydriodide, C¹⁰H¹⁶.HI, is formed, which does not solidify on cooling, and is decomposed by heat or by exposure to light. When the alcoholic solution of this hydriodide is heated with silver cyanide, and the product is boiled with potash, ammonia is given off, and a brown mass is formed, together with a small quantity of a non-volatile amorphous acid, soluble in ether. Hesperidene, heated with *phosphorus pentasulphide*, yields cymene (Wright, *Chem. Soc. J.* 1873, 549).

On Nitrosohesperidene, see TERPENES, NITROSO-.

HESPERIDIN, C²²H³⁶O¹². This substance, discovered by Lebreton (iii. 150), exists in many fruits of the genus *Citrus*. It is best prepared from the dry unripe bitter oranges of commerce (*Poma aurantii immaturi*). The fruit is exhausted with water, and the residue is treated with a mixture of equal parts of water and alcohol containing one per cent. of caustic potash. On adding hydrochloric acid to this solution, impure hesperidin separates out, and may be dissolved in potash-solution of 5 per cent. On adding alcohol a resinous mass is deposited, and from the clear liquid almost pure hesperidin separates on adding hydrochloric acid. To obtain it quite pure it must be boiled with water containing acetic acid.

Hesperidin crystallises from water, alcohol, or dilute acids in white microscopic needles, and acids precipitate it from an alkaline solution in globular masses. It is almost insoluble in cold water, and dissolves in 500 parts of boiling water. It dissolves more freely in alcohol and hot acetic acid, but is insoluble in ether, benzene, and volatile oils. It is not decomposed by dilute acids, and does not reduce an alkaline copper-solution. Its solution in dilute potash becomes yellow and orange-coloured on standing; and on evaporating it to dryness and treating the residue with dilute sulphuric acid, it turns red and afterwards violet. Hesperidin fused with potash yields protocatechuic acid (E. Hoffmann, *Ber. Ber.* ix. 26).

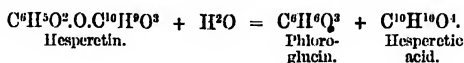
According to Paternò a. Briosi (*Gazz. chim. ital.* 1876, 169) hesperidin melts at 243°–245°, which is nearly the melting point of limonin (244°). It is decomposed by evaporation to dryness with ammonia, does not unite with picric acid, acetyl chloride, or baryta. It dissolves readily in aniline, and the solution mixed with ether deposits spherical groups of crystals the composition of which has not yet been determined.

Hesperidin is a glucoside, and is resolved by dilute acids into glucose and hesperetin, C¹²H¹⁸O⁶:



Hesperetin, C⁶H¹⁰O³.O.C¹⁶H²⁴O³, when purified by crystallisation from ether, forms white crystals melting at 223° and having an intensely sweet taste. It is soluble in cold water, nearly insoluble in alcohol; dissolves in alkalis, and is not

extracted from the solution by ether; gives a brown-red coloration with ferric chloride; is precipitated by lead acetate. Heated to 100° with potassium hydroxide, it is resolved almost quantitatively into hesperetic acid and phloroglucin:



Heated with water to 250° in a sealed tube, it yields a product having a strong smell of vanilla (Hoffmann).

Hesperetic acid, $\text{C}^{10}\text{H}^{10}\text{O}^4$, is likewise formed by the action of alkalis on hesperidin, and it may be purified by conversion into the soluble calcium salt, removal of colouring matters with lead acetate, reprecipitation with acetic acid, and crystallisation from alcohol. It melts at 225°, and sublimes at 223°, being partly decomposed at the same time, with formation of a body smelling like vanilla. By fusion with potash it is resolved into acetic and protocatechuic acids:



The substance called *Hesperidin* by de Vrij, and obtained from the aqueous portion of the residue left on distilling the flowers of *Citrus decumana*, is in reality the body called by Hoffmann aurantiin (p. 136). A body prepared by de Vrij from orange-peel (*Albedo cort. aurans*) is, according to Hoffmann, pure hesperidin. The following is a comparison of the composition and properties of hesperidin with those of allied glucosides.

	Composition	Melting point	Phenol reaction
Hesperidin	$(\text{C}^{22}\text{H}^{26}\text{O}^{12})$	245°	brown-red
Aurantiin	$\text{C}^{23}\text{H}^{26}\text{O}^{12} + 4\text{H}^2(\text{O})$	171	"
Murrayin	$\text{C}^{18}\text{H}^{22}\text{O}^{10}$	170	blue-green
Limonin	?	244	?

HESPERISIC ACID. See HESPERIDENE (p. 1028).

HESSITE, Ag²Je. See TELLURIUM.

HETEROMORPHITE. According to Pisani (*Compt. rend.* lxxxiii, 747) this mineral occurs at Alsberg in Westphalia, mixed with brown blende, mostly massive; in cavities also, apparently in monoclinic crystals. Sp. gr. = 5.59–5.73.

S	Sb	Pb	Zn
19.90	31.20	47.86	0.60 = 99.56.

Pisani represents these numbers by the formula $\text{Pb}^2\text{Sb}^2\text{S}^{10} = 7\text{PbS}.4\text{Sb}^2\text{S}^3$. H. Rose assigned to heteromorphite the formula $\text{Pb}^2\text{Sb}^2\text{S}^3 = 2\text{PbS}.2\text{Sb}^2\text{S}^3$ (iii, 151).

HEUBACHITE. A hydrated oxide of nickel and cobalt, occurring in extremely thin soot-like deposits, or more rarely in the form of dendritic foil and fine globular aggregations, on clefts in barytes, at the St. Anton Mine in the Heubachthal, near Wittichen. Colour deep-black; the streak exhibits a semi-metallic lustre. Hardness = 2.5. Sp. gr. 3.44. It is infusible before the blow-pipe, but dissolves in hydrochloric acid with evolution of much chlorine, the solution having a deep bluish-green colour, but changing into rose-red on dilution with water. Chemical composition as follows:—

CoO	NiO	Fe ² O ³	MnO ²	H ² O
65.50	14.50	5.13	1.50	12.59 = 99.22.

Heubachite is a very recent formation, being found only on clefts in barytes, and cementing together fragments of quartz and felspar, which have arisen from the disintegration of the neighbouring vein-rocks and been carried by the action of water into the barytes clefts. This water no doubt contained the constituents of heubachite in solution in the form of carbonates. Heubachite is found occurring under exactly similar circumstances at the Eberhard mine near Alpirsbach in the Swabian Schwarzwald (Sandberger, *Jahrb. f. Min.* 1877, 299).

HEULANDITE. This mineral, from the conglomerates of a South African melaphyre, was found by E. Cohen (*ibid.* 1875, 116) to contain:

SiO ²	Al ² O ³	CaO	K ² O	Na ² O	Loss by ignition
59.53	16.82	6.95	0.32	1.42	15.30 = 100.34.

HEXACETYLMAANNITE. See MAANNITE.

HEXACROLEIC ACID, $C^{18}H^{24}O^6$. An acid polymeric with acrolein, produced by dropping that liquid into an alcoholic solution of potash (iii. 150); found also among the products obtained by heating acrolein hydrochloride with sodium ethylate (p. 42 of this Supplement).

HEXAGONITE. A variety of tremolite (iii. 169) from Edwards, St. Lawrence County, New York, first described by Goldsmith, who placed it in the beryl group. König, however (*Jahrb. f. Min.* 1877, 202), finds that the crystals are monoclinic, and exhibit the combination $OP.\infty P$, tabular through OP . The prism-angle, $124^\circ 39'$, agrees closely with that of tremolite ($124^\circ 30'$). Cleavage prismatic and imperfect, parallel to OP . Hardness = 6.5. Sp. gr. = 2.996. Colour, white or violet. Lustre strongly vitreous. Melts with difficulty before the blow-pipe to a white enamel. Gives the reaction of manganese with borax. Chemical composition as follows:

SiO^2	MgO	CaO	Na^2O	MnO	Al^2O^3 a. Fe^2O^3
58.20	24.14	12.20	1.90	1.37	1.40 = 99.21

HEXANE, C^6H^{14} . Normal hexane (b. p. 68° – 70°), from Pennsylvanian petroleum, is converted by the action of chlorine chiefly into two hexyl chlorides (b. p. 120° – 134°), which when saponified with alcoholic potash yield a mixture of two hexylenes (b. p. 68° – 70°) not separable by distillation. But on passing a stream of hydrochloric acid gas through a mixture of these hexylenes with strong hydrochloric acid, a hexyl chloride gradually separates, boiling, with decomposition, at 116° – 118° ; and the remaining portion of the hexylene, heated with hydrochloric acid to 130° – 140° for ten or twelve hours, yields a hexyl chloride boiling at 122° – 124° . The first-mentioned chloride (b. p. 116° – 118°) heated with acetic acid and lead acetate, is converted into an acetic ether, yielding by saponification a small quantity of the corresponding hexyl alcohol. This alcohol, however, is much more readily obtained by similar treatment of the hydriodide produced by agitating the mixture of hexylenes above mentioned with concentrated hydriodic acid. It boils at 125° – 129° , smells like peppermint-oil, and is converted by a strong solution of chromic acid into a ketone boiling at 121° – 124° , and yielding by further oxidation, acetic and probably also propionic acid.

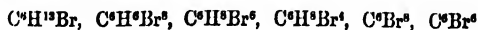
The chloride boiling at 122° – 124° is for the most part converted by heating to 120° with lead acetate and acetic acid, into an acetic ether yielding by saponification another hexyl alcohol, which boils at 132° – 137° , and is oxidised by chromic acid, even at ordinary temperatures, to a ketone boiling at 124° – 126° , and converted by further oxidation into a mixture of acids consisting chiefly of acetic and butyric acid: hence this alcohol appears to be methyl-butyl-carbinol, $CH^3.CHOH.C^4H^9$ (Morgan, *Chem. Soc. J.* 1875, 301).

These results seem to show that the action of chlorine on normal hexane gives rise only to secondary chlorides, whereas Schlorlemmer (*2nd Suppl.* 645), by chlorination of normal hexane (prepared by the action of nascent hydrogen on methyl-butyl iodide), obtained a primary as well as a secondary chloride.

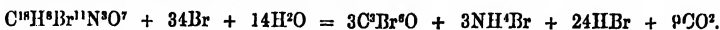
When bromine-vapour is passed into the vapour of boiling normal hexane, in daylight, substitution-products are formed, which are partly decomposed by distillation. The portion which distils without decomposition consists of a hexyl bromide, the alcohol from which is converted by oxidation into acetic and normal butyric acids, and therefore consists of methyl-butyl-carbinol. In like manner normal heptane yields a bromide convertible into methyl-pentyl carbinol. Hence it appears that the action of bromine on normal paraffins gives rise only to secondary bromides, $CH^3.CHBr.C^mH^{2m+1}$, or that the methyl groups which are present in these hydrocarbons, and are readily attacked by chlorine, are not touched by bromine at all.

In addition to the secondary bromides, other products are formed which, on distillation, either decompose completely, or are resolved into hydrobromic acid and non-saturated hydrocarbons, which are probably olefines (Schorlemmer, *Phil. Trans.* 1878, p. 1).

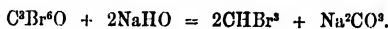
More highly brominated derivatives are obtained by heating normal hexane with bromine to higher temperatures in sealed tubes. At 130° – 140° the compound C^6Br^2 is formed, and this at a higher temperature is resolved into perbromobenzene, C^6Br^6 , and free bromine. If the heating at 130° – 140° be not too long continued, the crystalline compound, $C^6H^2Br^4$, is likewise obtained. At 120° – 125° this latter is the chief product, mixed however with $C^6H^4Br^2$ and C^6H^6Br . The brominated derivatives of hexane now known are:



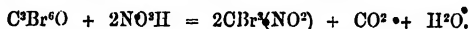
HEXBROMACETONE, C^3Br^6O (Weidel a. Grüber, *Ber.* x. 1147). This compound is formed by the action of bromine on a very dilute aqueous solution of the hydrochloride or hydrobromide of triamidophenol, $C^6H^2(NH^2)^3OH$, or on bromodichromazin, $C^6H^2Br^{11}N^3O^7$, the first product of the action of bromine on these salts, this body being suspended in water and bromine added to the liquid. At ordinary temperatures the reaction takes several hours to complete, but at 100° in sealed tubes it is completed in a few minutes. The hexbromacetone separates on cooling in lustrous scales, and may be purified by crystallisation from chloroform, from which it separates in large strongly-refracting monoclinic crystals. Its formation from bromodichromazin may be represented by the equation—



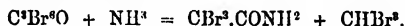
Hexbromacetone is absolutely insoluble in water, whether cold or boiling, but dissolves easily and without alteration in chloroform, carbon disulphide, benzene, and pure ether. It likewise dissolves in alcohol, either aqueous or absolute, but is at the same time partly decomposed, a small portion of it separating out unaltered as the alcohol evaporates, while the greater portion is converted into a red-brown oil smelling like chloroform. The ethereal and alcoholic solutions are neutral. The crystals are tasteless, but excite after some time a persistent burning sensation on the tongue. Hexbromacetone melts at 107° – 109° , in the dry state; below 100° , when immersed in water. At a higher temperature it decomposes, only a small portion subliming unchanged. When boiled with a caustic alkali it yields bromoform and an alkaline carbonate:



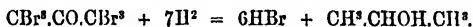
It is decomposed in a similar manner when heated with water to 180° . It dissolves in boiling nitric acid, and separates out unchanged on cooling; but when the two are heated together at 150° , bromopierin is formed, with evolution of carbon dioxide:



Dry ammonia-gas passed over hexbromacetone converts it quantitatively into tribromacetamide and bromoform:



On adding water to a solution of hexbromacetone in methyl alcohol till the compound begins to separate, and then adding sodium-amalgam, pseudopropyl alcohol is formed:

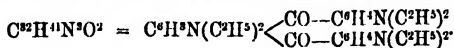


HEXBROMODIPHENYLAMINE. See BENZENES, PHENYLAMIDO- (p. 208).

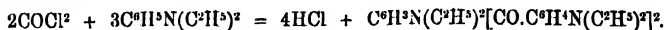
HEXBROMONAPHTHALENE, $C^{10}H^2Br^6$, is prepared by dropping bromine containing iodine, but free from chlorine, on naphthalene, which is kept cool, then heating the product with excess of bromine in a sealed tube, first to 80° – 100° (as long as hydrogen bromide escapes on opening the tube), afterwards continuing the heating for twenty or thirty hours, and raising the temperature from 50° to 60° till it finally rises to 350° – 400° . Hexbromonaphthalene is insoluble in alcohol and in ether, moderately soluble in hot benzene, toluene, chloroform, and aniline; crystallises and sublimes in slender needles; melts at 245° – 246° , resolidifies at 200° – 195° , and volatilises without decomposition (E. Gessner, *Ber.* ix. 1505).

HEXCHLORETHANE, C^2Cl^6 . This compound reacts with aluminium iodide in such a manner as to form aluminium chloride, tetrachlorethylene, and free iodine, together with an amorphous carbon compound containing iodine (Gustavson, *Ber.* ix. 169).

HEXETHYL-TRIAMIDOBENZOYL BENZENE,



This compound is formed, together with triethyl-diamidobenzophenone, $CO[C^6H^4N(C^2H^5)^2]^2$, by heating diethyl-aniline with carbonyl chloride in a sealed tube to 120° :



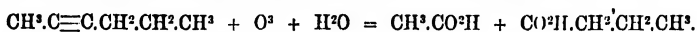
The product is boiled with water to remove excess of diethylaniline, and the undissolved residue, after washing on a filter, is treated with hydrochloric acid, which

dissolves the tetrethyl-diamidobenzophenene, and leaves the hexethyl-triamidobenzoylbenzene.

The latter body crystallises from alcohol in fine crystals melting at about 170° , and belonging, according to Arzruni's measurements, to the triclinic system. They are tabular in the direction of the base c , and exhibit a right and left hemiprism m and m' , together with a tetartopyramid o , between m and c (truncation of the acute edge). Angles of the normals, $c : m' = 58^{\circ} 19'$; $c : m = 63^{\circ}$; $o : c = 61^{\circ} 55'$ (Michler, a. Gradman, *Ber.* ix. 1912).

HEXYDROBENZENE, HEXHYDROTOLUENE, &c. See BENZENE (p. 160).

HEXINE, C^6H^{10} . *Hexylene*.—A modification of this hydrocarbon, most probably having the constitution $CH^3.C \equiv C.CH^2.CH^2.CH^3$, is obtained by heating monobromhexylene (derived from mannite hexylene) with alcoholic potash in sealed tubes, at 170° for twelve hours, about one third of the bromide then remaining undecomposed. The hydrocarbon is a colourless mobile liquid, having a pungent, disagreeable odour. It is optically inactive, and its sp. gr. is 0.7494 at 0° , and 0.7377 at 13° , referred to water at 0° . It remains liquid at -20° , and boils between 80° and 83° ; it is miscible in all proportions with alcohol, ether, chloroform, carbon bisulphide, benzene, light petroleum, and glacial acetic acid; dissolves in sulphuric acid, sp. gr. 1.83 ; does not produce a precipitate in ammoniacal solutions of silver or cuprous salts. By boiling with chromic acid mixture it is oxidised to butyric, acetic and carbonic acids. The formation of acetic and butyric acids is represented by the equation:

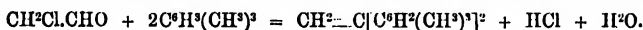


The carbonic acid is formed (as was proved by direct experiment) by further oxidation of a portion of the butyric acid.

Hexine dibromide, $C^6H^{10}Br^2 = CH^3.CBr = CBr.CH^2.CH^2.CH^3$, produced by the direct union of bromine and hexine, is an optically inactive liquid, of a pale-yellow colour. Sp. gr. 1.6977 at 0° , 1.5543 at 100° . It does not solidify at -20° , begins to decompose at 130° . Bromine acts slowly upon it, with evolution of hydrobromic acid, and formation of a heavy yellow oil (probably a mixture of $C^6H^{10}Br^1$ and $C^4H^{12}Br^2$), which has a density of 2.1625 at 0° , thickens to a syrup at -15° , and begins to decompose at 160° (Hecht, *Ber.* xi. 1050).

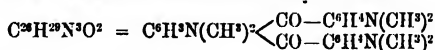
HEXMETHYLDIAMIDOBENZOIC ACID, $C^6H^4(CH^3)^2N^2O^2(OH)^2$. See BENZOIC ACIDS (p. 274).

HEXMETHYL-ISOSTILBENE, $C^{12}H^{24} = CH^2 = C[CH^2(CH^3)^2]^2$, is formed by the action of sulphuric acid on a mixture of mesitylene and monochloraldehyde:



It is an oily liquid, boiling at a high temperature and readily attacked by bromine (E. Hopp, *Ber.* vii. 1418).

HEXMETHYL-TRIAMIDOBENZOYL BENZENÉ,



is prepared, like the corresponding ethyl-compound (p. 1031), by heating dimethylaniline in a sealed tube with liquid carbonyl chloride (Michler, *Ber.* ix. 716); also by passing gaseous carbonyl chloride (phosgene) into boiling dimethylaniline as long as it is absorbed (Michler a. Dupertuis, *ibid.* 1899). The compound forms monoclinic crystals having the axial ratio $a : b : c = 0.5865 : 1 : 0.7138$. Angle $ac = 125^{\circ} 18'$. Observed faces $\infty R2$, $\infty R \infty$, P , $P \infty$, 0 . Angle $P : 0P = 75^{\circ} 33'$; $P : P = 53^{\circ} 38.5'$. $\infty R2 : \infty R2 = 65^{\circ} 6.5'$ (Groth).

HEXNITRODIPHENYLAMINE, $C^{12}H^5N^7O^{12} = NH \begin{matrix} \diagup C^6H^2(NO^2)^3 \\ \diagdown C^6H^2(NO^2)^3 \end{matrix}$. *Dipicrylamine* (Gnehm, *Ber.* vii. 1399).—This compound is formed by heating diphenylamino, or methyl-diphenylamine, with nitric acid as long as red vapours are given off; in the latter case the methyl-group is removed by oxidation. The product is washed with water and crystallised from alcohol or glacial acetic acid, from the latter of which it separates in light yellow prisms melting at 233° – 234° . It forms salts with bases. The *barium salt*, $C^{12}H^3BaN^7O^{12}$, crystallises in rhombohedrons having a fine red colour; the *ammonium salt* forms red laminæ.

Hexnitrodiphenylamine constitutes the yellow dye known as 'aurantia' (Gnehm, *Ber.* ix. 1245, 1557).

HEXNITRO-INOSITE. See INOSITE.

HEXNITRO-MANNITE. See MANNITE.

HEXOIC ACIDS, $C^6H^{12}O_2 = C^5H^{11}.CO^2H$. *Caproic acids.*—Of the eight possible modifications of this acid, five are at present known, viz.:

(1). **Normal Hexoic or Caproic, Pentyl-formic, Butyl-acetic or Propyl-propionic Acid,** $CH^3.CH^2.CH^2.CH^2.CH^2.CO^2H$. Formed by saponification of normal pentyl cyanide, and found among the products of the butyric fermentation of sugar; produced, also, together with other acids of the fatty series, by the oxidation of albuminous substances and of fatty acids of higher atomic weight. Respecting its physical properties and those of its barium salt, calcium salt, and ethylic salt, see table (p. 378). It is oxidised by nitric acid to acetic and succinic acids (Erlenmeyer, Siegel u. Belli. *Ber.* vii. 696). Respecting its conversion into normal valeric acid, see VALERIC ACIDS.

(2). **Isohexoic or Isocaproic, Isopentyl-formic, Isobutyl-acetic, or Isopropyl-propionic Acid,** $(CH^3)^2CH.CH^2.CH^2.CO^2H$, is formed by saponification of isopentyl or amyl cyanide (from fermentation amyl alcohol); also by hydrogenation of pyroterebic acid, $C^6H^{10}O_2$, namely by heating 2.5 to 3 grams of that acid to 180° – 190° for six to eight hours with 15 grams of hydriodic acid saturated at 0° , and 0.5 gram of red phosphorus. The acid thus prepared agrees exactly in its properties with the caproic acid from amyl cyanide; boiling at 199° – 199.5° (mercury-column wholly in the vapour), and remaining liquid at -18° . Its calcium salt forms long colourless prisms having the composition $(C^6H^{11}O_2)^2Ca + 3H_2O$, and not much more soluble in hot than in cold water. 100 parts of the solution saturated at 21° contain 4.58 parts of anhydrous salt. The barium salt, $(C^6H^{11}O_2)^2Ba + H_2O$, crystallises less easily. 100 parts of its solution saturated at 17.5° contain 19.11 parts, and at 22° the same quantity of solution contains 18.4 parts of the anhydrous salt (W. C. Williams, *Ber.* vi. 1098; Fittig u. Mielck, *ibid.* vii. 649; Mielck, *Liebig's Annalen*, clxxx. 45).

(3) and (4). **Diethylacetic Acid,** $(C^2H^5)^2CH.CO^2H$, and **Methyl-isopropyl-acetic Acid,** $\begin{matrix} (CH^3)^2CH \\ | \\ CH^3 \end{matrix} CH.CO^2H$ (A. Saytzeff, *Ber.* xi. 511). *Diethylacetic acid*, obtained from the product of the action of potassium cyanide on diethyl-carbinyl iodide, is a colourless liquid boiling at 190° . It has a pleasant odour, and is only slightly soluble in water. Sp. gr. at $18^\circ = 0.9196$.

Methyl-isopropylacetic acid, obtained from the product of the action of potassium cyanide on methyl-isopropyl iodide, or amylene hydriodide, closely resembles the preceding acid. It boils at 193° , and its sp. gr. at 18° is 0.9279.

The sp. gr. of *ethylic di-ethylacetate* (b. p. 151°) is 0.8686 at 18° , and that of *ethylic methylpropylacetate* (b. p. 153°) is 0.867 at the same temperature.

The silver salts of these acids are deposited from hot saturated solution, on cooling, in needle-shaped crystals. *Silver di-ethylacetate* is less soluble in cold, but more soluble in hot water than its isomeride.

The barium salts are easily soluble in water and in alcohol. *Barium di-ethylacetate* is crystalline, but *barium methylpropylacetate* forms a thick syrup which dries to a gum-like mass. The solubility of *calcium di-ethylacetate* in water increases with the temperature. *Calcium methylpropylacetate* is less soluble in hot than in cold water. The lead salts are very soft and easily fusible.

The zinc salts dissolve in alcohol; they are more soluble in cold than in hot water. Ferric chloride forms a yellow precipitate with ammonium di-ethylacetate, insoluble in excess, whilst with the methylpropylacetate it produces a flesh-coloured precipitate soluble in excess of the reagent.

(5). **Ethyl-dimethylacetic Acid,** $(CH^3)^2(C^2H^5)C.CO^2H$ (Wischnegradsky, *Liebig's Annalen*, clxiv. 56; clxxviii. 103). To prepare this acid, ethyldimethyl-carbinyl iodide is heated with potassio-mercuric cyanide, and the product repeatedly fractionated by distillation, whereby the corresponding cyanide is obtained as a liquid, which boils at 128° – 130° , and solidifies in a mixture of snow and salt; and on heating this cyanide with fuming hydrochloric acid in sealed tubes for six days to 100° , and then for two days to 120° , ethyl-dimethylacetic acid is obtained as a liquid which may be purified by drying and rectification. The same acid is produced by oxidation of methyl-katapentyl ketone, $CH^3.CO.C(CH^3)^2(C^2H^5)$, and ethyl-katapentyl ketone.

Ethyl-dimethylacetic acid boils at 184° – 186° , and solidifies in a freezing mixture to a laminated mass of slender needles melting at -14° . It is insoluble in water and has a faint fatty odour. Both in the free state and in its salts it resembles trimethyl-

acetic acid. The *neutral sodium salt* is very soluble and does not crystallise; its solution, mixed with the free acid, deposits a sparingly soluble *acid salt* in stellate groups of needles. The *barium salt*, $(C^6H^{11}O^2)Ba.5H^2O$, crystallises from an aqueous solution saturated at the boiling heat, as a laminar mass; from a less concentrated solution in large transparent plates. It effloresces in dry air, dissolves easily in water, but is not easily wetted thereby. It shows a tendency to the formation of super-saturated solutions, and gives off a portion of its acid when its solution is boiled. The *calcium salt* forms shining slender needles very soluble in water. The *magnesium salt* is a gummy mass. The *zinc salt*, $(C^6H^{11}O^2)_2Zn$, separates as a white bulky precipitate on mixing slightly warmed solutions of the sodium salt and zinc sulphate, and crystallises from solution in a large quantity of water by slow evaporation in transparent prisms. Its aqueous solution, saturated at ordinary temperatures (containing 2.4 per cent. of anhydrous salt at 16°), becomes turbid when heated, and gradually stiffens, in consequence of the separation of a translucent basic salt, but becomes clear and fluid again on cooling. The *silver salt*, $C^6H^{11}O^2Ag$, is a white precipitate more soluble in hot than in cold water, and separates on cooling in slender needles having a silky lustre; blackens slightly when exposed to light. The *lead salt* is a bulky precipitate which, when boiled with water and a small quantity of the free acid, yields slender needles of an *acid salt*. The *copper salt* is obtained by precipitation as a greenish-blue powder; it dissolves in alcohol, and crystallises therefrom in dark green very efflorescent prisms.

A *trichlorhexoic acid*, $C^6H^3Cl^3O^2$, the exact constitution of which is not known, is produced by the action of fuming nitric acid on hexyl chloral (p. 1036), the two liquids being kept in contact for twenty-four hours, and the product poured into about eight times its volume of water. The trichlorhexoic acid then separates as an oil which solidifies after a time, and may be crystallised from a mixture of benzene and petroleum. The acid melts at 61° , and is almost insoluble in water, but very soluble in alcohol, ether, and benzene, less so in petroleum. It is strongly acted upon by zinc-dust in presence of water, and if hydrochloric acid be then gradually added, the surface of the zinc in the course of a few days becomes covered with long, flat needles of a *hexylenic acid*, $C^6H^{10}O^2$, metameric with hydrosorbic, pyroterebic, and ethylcrotonic acids. It melts at 39° , is almost insoluble in water, but very soluble in alcohol, ether, benzene, and petroleum (Pinner, *Ber.* x. 1052).

HEXYL ALCOHOLS, $C^6H^{14}O = C^6H^{13}.OH$. Of these alcohols, seventeen are possible and eight are known, viz., two primary, three secondary, and three tertiary.

PRIMARY. (1). **Normal Hexyl Alcohol**, $CH^3.CH^2.CH^2.CH^2.CH^2.CH^2OH$, is obtained: 1. From the essential oil of *Heracleum giganteum*, which contains hexyl butyrate (2nd Suppl. 616). 2. Together with the secondary alcohol, methyl-butyl carbinol, by treating normal hexane, from American petroleum, with chlorine, converting the resulting mixture of primary and secondary hexyl chlorides into the corresponding acetates, and distilling the latter with potash. The mixed alcohols thus obtained cannot be separated by distillation, but they yield by oxidation the corresponding products, viz., normal caproic acid and methyl-butyl ketone (Schlorlemmer, 2nd Suppl. 645). 3. By the action of sodium-amalgam on normal caproic aldehyde (Lieben a. Rossi, *Liebig's Annalen*, cxxxiii. 178; Lieben a. Janacek, clxxviii. 126). The following are the properties of the hexyl alcohol prepared by the last process, and of some of its ethers, as determined by Lieben a. Janacek (compare 2nd Suppl. 616).

	Alcohol	Iodide	Bromide	Chloride	Ethylate
Boiling point . .	157.2° at 740.8 mm.	181.4° at 746.8 mm.	155.5° at 743.8 mm.	133°	$134^\circ-137^\circ$
Specific Gravity	0.833 at 0°	1.4607 at 0°	1.1935 at 0°		
	0.8204 at 20°	1.4363 „ 20°	1.1725 „ 20°		
	0.8107 „ 40°	1.4178 „ 40°	1.1561 „ 40°		

(2). **Isohexyl Alcohol**, $CH(CH^3)_2.CH^2.CH^2.CH^2OH$. This is probably the constitution of the hexyl alcohol which Faget obtained from fusel oil. B. p. about 150° . Converted by oxidation into ordinary caproic acid.

SECONDARY HEXYL ALCOHOLS.

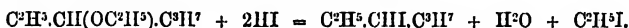
(1). **Methyl-butyl Carbinol**, $\text{CH}_3\text{CH(OH)(CH}_2\text{)}_3\text{CH}_3$. *β -Hexyl-Alcohol*.—This is the alcohol whose iodide is produced by boiling mannito or dulceto with highly concentrated hydriodic acid (iii. 154). It is likewise obtained, as already described (p. 1034), from the mixture of chlorides produced by the action of chlorine on petroleum hexano. The alcohol boils at 137° , the iodide at 167.5° (bar. at 752 mm.); the chloride at about 120° (Wanklyn a. Erlenmeyer); 122° – 124° (Morgan).

Methyl-butyl Thiocyanate, or *β -Hexyl Thiocyanate*, $\text{S} \left\{ \begin{smallmatrix} \text{CN} \\ \text{BC}_6\text{H}_{13} \end{smallmatrix} \right.$, is prepared by boiling equal parts of the alcohol and potassium thiocyanate—the latter dissolved in the smallest possible quantity of ethyl alcohol—for an hour on the water-bath in a reflux-apparatus. When precipitated by water, dried, and rectified, it forms a liquid boiling at 206° – 207.5° and having an alliaceous odour.

The corresponding *Isothiocyanate*, or *β -Hexyl-thiocarbimide*, $\text{N} \left\{ \begin{smallmatrix} \text{CS} \\ \text{BC}_6\text{H}_{13} \end{smallmatrix} \right.$, is obtained by boiling β -hexylamine with ethyl alcohol and carbon disulphide, evaporating off the alcohol, and heating the residue with solution of mercuric chloride. It is a colourless liquid, having a specific gravity = 0.9253, and boiling at 197° – 198° . When heated with strong sulphuric acid it is reconverted into the amine, with separation of sulphur (Uppenkamp, *Ber.* viii. 55).

5. **Methyl-katabutyl Carbinol**, or **Pinacolyl Alcohol**, $\text{CH}_3\text{CH(OH).C(CH}_3\text{)}_3$, formed by the action of nascent hydrogen on the corresponding ketone (pinacolin), is a liquid having a density of 0.8317 at 0° , boiling at 120.5° , and solidifying at low temperatures to a mass of long silky needles, which melts at $+4^\circ$. By oxidation with chromic acid mixture it yields the ketone. See further 2nd Suppl. 982, where this alcohol is formulated as a tertiary alcohol, dimethyl-isopropyl carbinol, $(\text{CH}_3)_2\text{COH—CH(CH}_3\text{)}_2$.

Ethyl-propyl Carbinol, $\text{C}_2\text{H}_5\text{CH(OH).C}_2\text{H}_5$, is formed: *a.* By the action of nascent hydrogen (water and sodium-amalgam) on ethyl-propyl ketone, prepared by distilling a mixture of butyrate and propionate of calcium (O. Völker, *Ber.* viii. 1019). *β .* The corresponding *iodide* is obtained by the action of hydriodic acid on diethylic ethyl oxide or ethyl-propyl-carbinyl ethylate (p. 746):

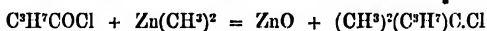


The iodide is then converted into the *acetate*, and the acetate by saponification into the alcohol (Lieben, *Liebig's Annalen*, cxxxviii. 1).

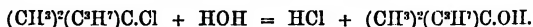
Ethyl-propyl ketone is a liquid boiling between 134.5° and 135.5° (corr.), and having a density of 0.8335 at 0° . By oxidation with chromic acid it is converted into propionic acid (Völker).

TERTIARY HEXYL ALCOHOLS.

Dimethyl-propyl, and **Dimethyl-isopropyl Carbinol**, $\text{C}_2\text{H}_5\text{C(OH)(CH}_3\text{)}_2$, are obtained by treating butyryl and isobutyryl chloride respectively with zinc-methyl, and decomposing the resulting chloride with water:



and



Dimethyl-propyl Carbinol, obtained in this manner by Butlerow, is a liquid resembling tertiary butyl alcohol; rather viscid; lighter than water, and somewhat soluble therein; having an alcoholic and camphorous odour; boiling at 115° (Butlerow), between 122.5° and 123.5° (Jawein, *Liebig's Annalen*, xciv. 254); not solidifying in a freezing mixture; oxidised by chromic acid mixture to acetic and propionic acid. The corresponding *chloride* is a liquid having a disagreeable odour, and boiling, with decomposition, at 100° .

Dimethyl-isopropyl Carbinol, $\text{CH(CH}_3\text{)}_2\text{C(OH)(CH}_3\text{)}_2$, after drying with baryta, distils over for the most part at 112° – 113° (Prianchnikow); at 117° (Pawlow). It is a colourless liquid, having a camphorous odour, perceptibly soluble in water, becoming viscid at -20° , and solidifying at -35° , in long, slender, white needles having a

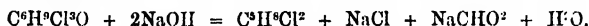
silky lustre. Sp. gr. = 0.8364 at 0°. Its expansion-coefficient for one degree between 0° and 50° is 0.00099. By oxidation with chromic acid mixture it yields acetone and a small quantity of acetic acid (Priazhnikow, *Bull. Soc. Chim.* [2], xvi. 303).

Friedel and Silva regard pinacolyl alcohol (*2nd Suppl.* 982) as dimethyl-isopropyl carbinol; but pinacolyl alcohol boils at 120.5°, and melts at +4°, whereas dimethyl-isopropyl carbinol boils at 112°–113°, and does not solidify till cooled to –35°. Moreover the mode of formation of pinacolyl alcohol, by the action of nascent hydrogen on pinacolin, which is a ketonic body, and its reconversion into that body by oxidation, show that it has the constitution of a secondary alcohol.

Methyl-diethyl Carbinol, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{COH}$, is obtained by acting on acetyl chloride, CH_3COCl , with zinc-ethyl, and treating the product with water. It boils at 120°; and yields by oxidation nothing but acetic acid. The corresponding chloride boils at 110°.

On the relations between the constitution of Hexyl Alcohols and their Boiling points, see HEAT (p. 945).

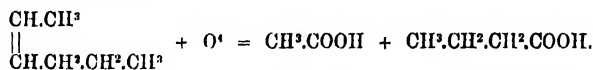
HEXYL CHLORAL, $\text{C}_6\text{H}_{11}\text{ClO} = \text{C}_6\text{H}_{10}\text{Cl} \cdot \text{CHO}$ (Pinner, *Ber.* x. 1052). This compound is separated by fractional distillation from the higher-boiling portions of crude butyl chloral (p. 50). It has a peculiar odour; distils undecomposed between 212° and 214°; is insoluble in water, but dissolves in alcohol, ether, and benzene. It does not unite either with water or with hydrocyanic acid. Its physiological action appears to be but feeble. Alkalis decompose it, producing a formate, a chloride, and a dichloropentylene:



Nitric acid converts it into a trichlorocaproic acid (p. 1034).

HEXYLENES, C_6H_{12} . On the hexylenes obtained by decomposition of the hexyl chlorides from normal hexane, see MORGAN (p. 1030).

Mannite Hexylene.—This modification is obtained by the action of potash on the hexyl iodide prepared by boiling mannite with concentrated hydriodic acid (iii. 152). It boils at 68°–70°. When oxidised by chromic acid it yields normal butyric, acetic, and carbonic acids; and the same products are obtained by oxidation of the corresponding glycol. This result shows that mannite hexylene has the constitution of propyl-methyl-ethylene:



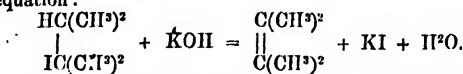
The carbonic acid is produced by further oxidation of a portion of the butyric acid (O. Hecht, *Ber.* xi. 1152, 1154).

The **dibromide**, $\text{C}_6\text{H}_{12}\text{Br}_2$, prepared by dropping bromine into this hexylene cooled to –17°, and purified by washing, first with dilute aqueous potash, then with water, and subsequent drying and rectification (whereby it is partly decomposed), is a faintly yellow liquid, having a density of 1.6058 at 0°, and 1.5809 at 19°, and boiling at 195°–197° under a pressure of 739.5 mm.

Monobromhexylene, $\text{C}_6\text{H}_{11}\text{Br}$, prepared by dropping bromine into the dibromide warmed in a vessel with ascending condenser, pouring the resulting distillate into water, and collecting the oil which sinks to the bottom, is, after drying and rectification, a slightly yellowish liquid having a density of 1.2205 at 0°, and 1.2025 at 15°, and boiling at 140°–141° (Hecht and Strauss, *Liebigs Annalen*, clxxii. 62).

A hexylene boiling at 66°–68°, doubtless identical with that just described, is obtained as a secondary product in the preparation of diethylic ethyl oxide, or methyl-propyl ethylate (p. 746).

Hexylenes from Tertiary Hexyl Alcohols (Jawein, *Liebigs Annalen*, cxcv. 253–264). 1. **Tetramethyl-ethylene**, $\text{C}^2(\text{CH}_3)^4$.—This compound is formed by the action of alcoholic potash on dimethyl-isopropyl-carbinyl iodide, in the manner shown by the following equation:



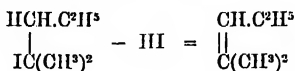
It boils at 73°, and unites directly with bromine, forming a solid **dibromide**, $\text{C}_6\text{H}_{12}\text{Br}_2$, which dissolves in alcohol, ether, and benzene. The ethereal solution deposits it in long needles, which melt with partial decomposition at 140°. The **hydriodide**, $\text{C}_6\text{H}_{12}\text{HI}$, boils at 140° and solidifies at –22°. The **hydrochloride**, $\text{C}_6\text{H}_{12}\text{HCl}$, boils

at 112° and solidifies at -14° . Tetramethyl-ethylene is completely oxidised to acetone by a 10 per cent. solution of chromic acid. Sulphuric acid at 60° converts it into a dihexylene, $C^{12}H^{24}$.

Pinacone, $C^8H^{14}O^2$, is probably tetramethyl-ethylene glycol, $C^2(CH^3)^4.H^2O^2$, inasmuch as pinacone-hydrate is formed by the action of baryta on the ether obtained by treating tetramethyl-ethylene bromide with silver nitrate (Pawlow, *Ber.* xi. 513).

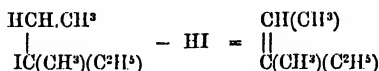
2. Ethyl-dimethyl-ethylene, $C^2H(CH^3)^2(C^2H^3)$. Of this hexylene there are two modifications, viz.: α . Having its two methyl-groups attached to the same carbon-atoms. β . Having these groups attached to different carbon-atoms.

α . This hexylene is obtained by the action of alcoholic potash on dimethyl-propyl-carbinyliodide:



When purified by boiling with sodium and subsequent fractional distillation, it boils at 65° – 67° , and has a density of 0.702 at 0° , 0.687 at 19° . Coefficient of expansion for 1° degree = 0.0017. By oxidation with chromic acid it yields chiefly acetic acid, propionic acid, and acetone.

β . The ethyl-dimethyl-ethylene, having its two methyl-groups attached to different carbon-atoms, is obtained in like manner from ethyl-dimethyl-carbinyliodide:



This hydrocarbon, first obtained by Tschakowsky, and further examined by Jawein, boils at 69.5° – 71° (bar. 760 mm. at 0°), and has a density of 0.712 at 0° ; 0.698 at 19° . Expansion-coefficient, for 1° 0.00116. By oxidation with chromic acid, which takes place very slowly—a portion of the hydrocarbon remaining unaltered even after several months contact with the acid at ordinary temperatures—it is converted into acetic acid, together with a small quantity of a ketone, probably methyl-ethyl ketone.

Polymerisation of Hexylenes.—The polymerisation of the two ethyl-dimethyl-ethylenes above described is best effected by agitating 1 volume of the hexylene with somewhat more than 2 volumes of a mixture of $SO^{11}H^2$ (2 pts.) and water (1 pt.), the vessel being immersed in a mixture of ice and salt, and the agitation continued till the whole of the hexylene is dissolved. On subsequently exposing the solution to the temperature of the air, an oily layer separated on the surface, of smaller volume than the hexylene employed. This layer was separated, purified by boiling with metallic sodium, and subjected to fractional distillation. The vapour-densities of the condensation-products thus obtained showed them to be dihexylenes.

α -Ethyl-dimethyl-ethylene, $C^2H^3.CH=C(CH^3)^2$, yielded a dihexylene boiling at 193° – 197° , and having a density of 0.795 at 0° , 0.786 at 19° . Expansion-coefficient for 1° = 0.00065.

β -Ethyl-dimethyl-ethylene, $CH^3.CH=C(CH^3)(C^2H^3)$, yielded a dihexylene boiling at 196° – 199° , and having a density of 0.809 at 0° ; 0.798 at 19° . Expansion-coefficient for 1° = 0.00080.

HIPPURIC ACID, $C^8H^8NO^3 = CH^2.NH(C^2H^3O).COOH$. Some of the derivatives of this acid have been examined by W. Conrad (*J. pr. Chem.* [2], xv. 241–260). He finds that *ethyl hippurate* melts at 60.5° , and distils, with partial decomposition, at temperatures above 180° ; according to Stenhouse (iii. 162), it melts at 44° . *Methyl hippurate* melts at 80.5° , and cannot be distilled at all (melts at 60° , and decomposes at 250° , Stenhouse). *Hippuramide*, $CH^2.NH(C^2H^3O).CONH^2$, formed by the action of ammonia on either of these ethers, melts at 183° . It is a weak base, and forms a crystalline hydrochloride.

The conversion of hippuric into *benzoglycollic acid*, $CH^2.O(C^2H^3O).COOH$, is most readily effected by the action of alkaline hypochlorites. Benzo-glycollic acid forms crystals melting at almost exactly the same temperature as benzoic acid (120°).

Nitrohippuric acid, $C^8H^8(NO^2)NO^2$, melts at 162° (at about 150° , Stenhouse), and is resolved by heating with fuming hydrochloric acid into glycocine and metanitrobenzoic acid (m. p. 141° – 142°).

Amidohippuric acid, $C^8H^8(NH^2)NO^2$, melts at 194° , forms crystallisable salts, and is resolved by heating with hydrochloric acid into glycocine and metamidobenzoic acid (m. p. 165°).

Diazohippuric acid, $C^9H^7N^2O^3$, formed by the action of nitrous acid on amido-hippuric acid, is converted by boiling with dilute sulphuric acid into *oxyhippuric acid*, $C^9H^7NO^4$ (Griess, 1st Suppl. 701); and this when boiled with strong hydrochloric acid is resolved into glycocine and meta-oxybenzoic acid melting at 197° (Conrad).

Formation of Hippuric Acid in the Animal Organism. A. Hoffmann (*Chem. Centr.* 1877, 409) finds from experiments on himself that, after the introduction of benzoic acid into the human organism, neither benzoic nor hippuric acid occurs in the perspiration. In one experiment in which benzoic acid alone was taken, that acid was found in the urine in addition to hippuric acid; whereas in another experiment, in which benzoic acid and glycocine were taken, no benzoic acid, but only hippuric acid, was detected in the urine, indicating that a combination of the benzoic acid with the glycocine had taken place. Experiments were also made by passing through fresh kidney removed from the body, defibrinated blood containing alanide, $(C^3H^7NO^2)$ —in addition to benzoic acid—whereby an acid (perhaps alanine-hippuric acid) was obtained in large white needles very different in appearance from the crystals of hippuric acid. Two experiments in which leucine and benzoic acid were passed together through the kidney, showed that either these bodies do not combine in the kidneys, or that the compound formed is decomposed by the treatment required for its separation. Further experiments showed that no hippuric acid was formed, when blood containing benzoic acid and glycocine and having its oxygen replaced by carbon oxide, was passed through a kidney removed from the body; but that the kidney, after blood saturated with carbon oxide had been passed through it for two hours, still possessed the power of forming hippuric acid from benzoic acid and glycocine when they were dissolved in oxygenated blood. A kidney removed from the body, and poisoned by passing blood containing quinine through it, showed little or no power of inducing the formation of hippuric acid from benzoic acid and glycocine: hence it would appear that this power is essentially a function of the living kidney.

The urine of dogs fed exclusively on animal food is generally supposed to contain little or no hippuric acid; according to Salkowski, however (*Ber.* xi. 500), such urine always contains a small quantity of that acid, not exceeding 1 part of hippuric acid to 129 parts of urea.

Formation of Hippuric acid in Herbivora.—Experiments on the formation of this acid in the organisms of herbivorous animals fed on different kinds of fodder have been made by Weiske, Kellner a. Wienand (*Chem. Centr.* 1876, 522, 536). The copious excretion of hippuric acid observed in animals fed on meadow-hay is due to the herbs mixed with the grass. Addition of common salt to the hay produces in the sheep a slight increase in the excretion of hippuric acid; addition of wheat, beans, or potatoes to the hay is followed by diminished excretion of hippuric acid. Benzoic acid added to the hay is almost wholly converted into hippuric acid; when, on the other hand, salicylic acid is mixed with the fodder, only a portion of it appears as salicyluric acid, the rest being excreted unaltered. When sheep were fed with peas, wheat, or oats, or with pea-straw, bean-straw, or unpeeled potatoes, no hippuric acid was found in their urine, but feeding with wheat or oat-straw was followed by excretion of that acid. When the animals were fed with meadow hay which had been treated with dilute sulphuric acid (1.25 per cent.), no hippuric acid was formed, and feeding with hay which had been macerated in potash-ley (1.25 per cent.), led to a diminished excretion of hippuric acid. Hofmeister, on the other hand, found that the treatment of hay with boiling water did not interfere with its property of forming hippuric acid, but that this property was completely destroyed by alcohol and by boiling potash solution of the strength of 3 per cent. (2nd Suppl. 647). Hence it may be inferred that the substance which gives rise to the formation of hippuric acid in the bodies of herbivorous animals is insoluble in boiling water, partially soluble in solution of potash (1.25 per cent.), and completely soluble in dilute sulphuric acid (1.25 per cent.), as well as in boiling alcohol and in boiling potash-solution of 3 per cent. Benzoic acid, added to the beans or potatoes with which the animals were fed, passed off unaltered, even when glycocine was likewise added to the fodder, but hippuric acid, added to beans or potatoes, was decomposed in the body.

For the numerical results obtained in these experiments, see *Zeitschrift f. Biologie*, xii. 241–265; *Chem. Soc. J.* 1877, i. 217–220.

HOMILITE. A mineral occurring, together with ordmannite and melinophane, at Stockoe near Brevig in Norway. The crystals, according to Nordenskiöld's measurement, are monoclinic, but the angle of the inclined axes differs so little from 90° that they may be very nearly represented as orthorhombic, with the axial ratio $a : b : c = 0.6362 : 1 : 0.6473$. Observed faces ∞P , ∞P_1 , ∞P_2 , P , \bar{P}_2 , \bar{P} , ∞ . Angle $\infty P : \infty P_2 = 160^\circ 48'$; $\infty P_2 : \infty \bar{P}_2 = 103^\circ 41'$; $\infty P_2 : \bar{P} \infty = 115^\circ 18'$; $\bar{P} \infty : P =$

116° (nearly); ∞ P : P = 139° 53'. Colour black to brownish-black. Lustre resinous to vitreous. Slightly transparent in thin fragments. Hardness = 5.5. Sp. gr. = 3.28. Fuses easily to a black glass; is readily decomposed by hydrochloric acid. Its analysis gave:

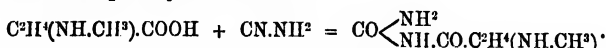
SiO ²	B ² O ³	Al ² O ³	Fe ² O ³	FeO	CaO	MgO	Na ² O	K ² O	Loss on ignition
31.875	18.085	1.50	2.145	16.25	27.275	0.54	1.09	0.41	0.41 = 99.56.

These numbers (after deducting Fe²O³) lead to the formula (CaO.FeO).2SiO².B²O³.

Homilite is very nearly related, both in form and in composition, to datolite (Paijkull, *Jahrb. f. Min.* 1877, 536).

HOMOCINCHONINE,* C¹⁰H¹²N²O. This, according to Hess (*Ber.* x. 2157), is the true composition of the base called 'cinchonine' by Skraup (p. 481).

HOMOCREATINE, C⁸H¹¹N²O². This base is formed by prolonged contact of the concentrated aqueous solutions of α -methylamidopropionic acid and cyanamide, in presence of a small quantity of ammonia:



It crystallises in monoclinic prisms, sparingly soluble in cold water and alcohol, easily in hot water, and turning brown at 150°–160°. The hydrochloride crystallises in needles, and forms double salts with zinc chloride and platinic chloride, the latter crystallising in octahedrons. Homocreatine, boiled with baryta-water, is decomposed, with evolution of ammonia (Lindenberg, *J. pr. Chem.* [2], xii. 244).

HOMODIMETHYLPROTOCATECHUIC or **HOMOVERATRIC ACID**. See VERATRIC ACID.

HOMO-OXYBENZOIC ACIDS and **ALDEHYDES**. See OXYTOLUIC ACIDS and ALDEHYDES.

HOMOPROTOCATECHUIC ACID. See VANILLIC ACID.

HOMOSALICYLIC ACID and **ALDEHYDE**. See OXYTOLUIC ACIDS and ALDEHYDES.

HOMOTEREPHTHALIC ACID. See TEREPHTHALIC ACID.

HOMOVERATRIC ACID. See VERATRIC ACID.

HOMOVANILLIC ACID and **VANILLIN**. See VANILLIC ACID and VANILLIN.

HONEY. The following analyses of honey from various sources are given by J. C. Brown (*Analyst*, 1878, 257):

	England	Wales	Nor-mandy	Ger-many	Greece	Lisbon	Jamnicen	Calif-ornia	Mexico
Water expelled at 100°	19.10	16.40	15.50	19.11	19.80	18.80	19.46	17.90	18.47
Water expelled at a high temperature and loss	7.60	6.56	4.95	11.00	7.80	6.66	7.58	8.13	10.03
Lævulose	36.60	37.20	36.88	33.14	40.00	37.26	38.19	37.85	35.96
Dextrose	36.55	39.70	42.50	36.58	32.20	31.91	35.21	36.01	35.47
Cane-sugar (?) { doubt-ful }	—	—	—	—	—	1.20	2.20	—	{ doubt-ful }
Wax, pollen, and insoluble matter	trace	trace	trace	trace	0.05	1.00	2.10	trace	trace
Mineral matter	0.15	0.14	0.17	0.17	0.15	0.14	0.26	0.11	0.07

The sp. gr. of honey is about 1.41, but varies slightly with the proportion of water.

A solution of 16.26 grams of crude honey in 100 c.c. water produces a deviation of -3.2° to -5° at 60° F. Greek honey produces a deviation of -5.5° . The same weight of dried honey in 100 c.c. water gives a deviation of about -4.8° .

* On page 489 of this Supplement, line 7, for 'Homocinchonine' read 'Homocinchonidine.'

Erlenmeyer a. von Planta (*N. Rep. Pharm.* xxiii. 610) also found the amount of water in six samples of honey to vary between 17·5 and 19·5 per cent. Senegal honey contained 25·6 per cent. water, and the amount of phosphoric acid (reckoned on the dry substance) was found to vary between 0·0123 and 0·883. The nectar of the flowers of *Fritillaria imperialis* contains nitrogen but no albumin, also phosphoric acid and a large quantity of gummy substances.

HOPS. *Composition.*—The following results, obtained from various samples of hops by extraction with ether, have been published by E. Porter (*Analyst*, 1876, 176). F denotes fine, M medium, L low quality:

	Moisture per cent.	Oil, resin, and bitter principle per cent.		Moisture per cent.	Oil, resin, and bitter principle per cent.
1. Worcester, F	4·02	14·98	7. Bavaria, M	9·97	13·08
2. Spalt, F	6·96	14·08	8. American, M	7·87	12·63
3. East Kent, F	6·15	13·60	9. Sussex, L	8·55	9·95
4. Worcester, M	8·10	13·35	10. Sussex, L	9·87	9·23
5. Kent, M	8·20	13·27	11. Poperingho, L	10·25	9·25
6. Sussex, M	7·05	11·75	12. Worcester, L	9·20	8·80

The ethereal residues from Nos. 1, 2, and 3 had a golden tint, all the others were of a greenish hue.

The tannin in hops is said to vary between 2 and 4·5 per cent. A good percentage of tannin doubtless increases the value of hops, as the tannin precipitates the mucilaginous matter in the beer; but the value depends mainly on the oil, resin, &c.

On the Tannin and Bitter Principle of Hops, see C. Etti (*Dingl. pol. J.* cxxviii. 491; *Chem. Soc. Jour.* xxxiv. 797).

Basic Constituents of Hops (Griessmayer, *Dingl. pol. J.* cexii. 67).—When the aqueous extract of hops is distilled with lime or calcined magnesia, and the distillate, which smells of ammonia and trimethylamine, is neutralised with hydrochloric acid, evaporated to dryness on the water-bath, and exhausted with alcohol, ammonium chloride remains undissolved, and the alcoholic solution, when evaporated, yields crystals of trimethylamino hydrochloride. On rendering the mother-liquor alkaline with potash, shaking it up with ether, and leaving the ethereal solution at the ordinary temperature in a shallow dish till the ether and the still remaining trimethylamino have evaporated, an alkaline residue is obtained which smells like conine, has a cooling not bitter taste, and exhibits the following reactions: *Platinic chloride*, after addition of alcohol and ether, produces a greenish-yellow precipitate; *strong sulphuric acid* and *potassium chromate*, a violet coloration; *fuming nitric acid*, a yellow colour, soon becoming green and dark-green, bluish on the edges, and the liquid after a short time becoming colourless; *tannic acid*, *silver nitrate*, *Fehling's solution*, and *mercuric chloride*, white precipitates; *auric chloride*, a white precipitate soluble in hydrochloric acid; *iodine solution* a brown, *bromine* a sulphur-yellow precipitate changing to orange and brown; *phosphotungstic acid*, a bulky yellow precipitate; *Nessler's reagent* produces the ammonia reaction. These reactions are attributed by Griessmayer to the presence of an alkaloid, which he designates as lupuline.

Sulphuring of Hops.—According to A. Schwarz (*Jahresb. f. Chem.* 1875, 1133), American hops are always sulphured. The effect of this operation is to alter the character of the essential oil, and render the resin less soluble in the beer-wort. Hence American beers deposit but very little resin during fermentation, and clarify but slowly.

To detect sulphurous acid in hops, Griessmayer (*Dingl. pol. J.* ccix. 227) adds to the filtered hop-extract a small quantity of sodium-amalgam and a few drops of hydrochloric acid, whereby, if the hops have been sulphured, hydrogen sulphide will be produced, and may be detected by lead-paper. According to A. Vogel (*ibid.* ccxv. 283), this reaction, which may likewise be produced with zinc and hydrochloric acid, may lead to erroneous conclusions regarding the sulphuration of hops, inasmuch as a large number of dried vegetable matters, for example mallow-leaves, lime-leaves, and many kinds of lupin, also give off hydrogen sulphide when treated with zinc and hydrochloric acid. With sodium-amalgam, however, these vegetable substances exhibit this reaction in a lower degree only, so that for the purpose in question it is more likely to give correct indications than zinc and hydrochloric acid.

HORBACHITE. According to A. Knop (*Jahrbuch f. Min.* 1873, 520), the nickel ore occurring in irregular lumps in the serpentinised gneiss of Horbach in the Schwarzwald, and hitherto regarded as a nickeliferous magnetic pyrites, has partly

the composition $4\text{Fe}^2\text{S}^3 \cdot \text{Ni}^2\text{S}^3$. That other ores of this locality have a different composition is shown by an older analysis by Rammelsberg (*Pogg. Ann.* cxxi. 360); analysis 6 below. Analyses 1-4 are by G. Wagner. The values required by Knop's formula are given under 5. Sp. gr. of horbachite = 4.43; of magnetic pyrites from Horbach = 4.7.

	1	2	3	4	5	6
S	45.87	46.07	45.68	—	45.9	40.03
Fe	41.94	41.62	42.15	42.13	42.8	55.96
Ni	11.52	12.44	—	—	11.2	3.86
Total	99.33	100.13	—	—	99.9	99.85

HORN. The composition of horn has been studied by H. Weiske (*Landw. Versuchs-Stationen*, xx. 35). A piece of stag's horn placed in water at the ordinary temperature imparts to the liquid after some time a deep red colour. The horn of the roebuck, however, does not produce this coloration. On evaporating the liquid to dryness, the colour changes to brown, and the dried residue, after treatment with common salt and acetic acid, shows under the microscope numerous crystals of hæmin. The dried extract contains 79.9 per cent. organic matter and 20.1 ash.

The ash consists of—

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	CO ₂	SO ₃	Cl
5.80	16.24	27.77	2.18	2.25	7.78	27.40	3.37	8.33 = 101.12.

To determine the amount of extractable matter, the powdered horn was digested first in ether and afterwards in water, and the extracts filtered, evaporated to dryness, and weighed. The following results were thus obtained:—

	Stag's horn	Roebuck's horn
Extracted by ether	0.26 per cent.	0.19 per cent.
„ water	5.76 „	4.55 „

The residue left, after extracting the ether and water, consisted of—

	Stag's horn	Roebuck's horn
Organic matter	36.32 per cent.	36.78 per cent.
Ash	63.68 „	63.22 „

The ash (allowing for carbonic acid expelled by burning) showed the following composition:—

	Stag's horn	Roebuck's horn
Lime	51.52 per cent.	51.51 per cent.
Magnesia	1.32 „	1.28 „
Phosphoric acid	39.31 „	39.08 „
Carbonic acid	4.60 „	4.88 „

The spongy part of the stag's horn amounts to about 24.94 per cent. of the total. An analysis of each part gave the following results:—

	Spongy part	Hard part
Extracted by ether	0.37 per cent.	0.11 per cent.
„ water	6.88 „	3.51 „

The residue left, after extraction with ether and water, consisted of—

	Spongy part	Hard part
Organic matter	49.89 per cent.	42.31 per cent.
Ash	50.11 „	57.69 „

The ash contained—

Lime	51.53 per cent.	51.58 per cent.
Magnesia	1.32 „	1.33 „
Phosphoric acid	39.43 „	39.79 „
Carbonic acid	4.25 „	4.03 „

For this examination a piece was cut from the middle of a large horn, whereas for the former analyses a complete antler was taken in each case, which may account for the difference in the percentage of ash. The proportion of ash to organic matter varies within certain limits, but the ash itself always shows very nearly the same composition.

HORNBLLENDE and **AUGITE**. G. vom Rath (*Pogg. Ann. Ergänzungsbd.* vi. 229; *Jahrb. f. Min.* 1876, 201) has analysed crystals of hornblende and augite formed by sublimation in blocks ejected from Vesuvius. No. 1 is yellow augite from a block thrown out in the eruption of 1872; 2 and 3 are from a block ejected in 1822; they exhibit all the characters of simultaneous formation, and are intergrown in parallel position. 4 is from a block of leucitophyr, probably of prehistoric origin.

	1. Yellow Augite.		2. Green Augite.		3. Brown Hornblende.		4. Black Hornblende.		
	SiO ^a	AlO ^a	FeO ^a	FeO	CaO	MgO	Na ^a O	Loss by ignition	Sp. gr.
1.	53·2	1·5	—	2·3	23·4	19·3	—	0·2 =	99·9
2.	48·4	5·6	—	9·5	22·9	13·7	—	0·3 =	100·4
3.	41·7	8·3	14·7	—	14·5	16·5	4·1	0·2* =	100
4.	41·7	9·5	17·7	—	13·4	13·4	4·0	0·3* =	100

Vom Rath has also analysed augite (1) and hornblende (2) intimately intergrown in an augitic labrador-rock on Monte Monzoni (*Zeitschr. geol. Ges.* xxvii. 361).

	SiO ^a	Al ^a O ^a	CaO	MgO	FeO	Sp. gr.
(1).	49·60	4·16	21·86	14·42	9·82 =	99·86
(2).	49·25	5·83	13·03	13·13	16·97 =	98·21

The following are analyses by E. E. Schmid (*Jahrb. f. Min.* 1876, 566) of hornblendes from the diorite of the Ehrenberg near Ilmenau.

SiO ^a	TiO ^a	Al ^a O ^a	Fe ^a O ^a	CaO	MgO	H ^a O	
43·26	0·82	12·18	16·44	10·93	10·84	2·57 =	97·04
46·35	0·45	19·07	13·10	10·39	4·19	2·53 =	96·08
43·19	0·55	19·55	19·03	11·69	2·62	3·18 =	99·81
46·07	trace	19·89	12·93	10·69	5·00	1·53 =	96·11

Specimens of the diorite rich in hornblende—so-called 'Hornblende slate'—gave by analysis:

SiO ^a	TiO ^a	Al ^a O ^a	Fe ^a O ^a	CaO	MgO	Na ^a O	K ^a O	H ^a O	
47·26	0·30	14·26	16·40	9·98	7·87	3·00	—	0·37 =	99·44
52·37	0·59	15·55	14·60	8·21	5·12	2·45	0·13	1·07 =	100·00

Varieties of Hornblende.—Actinolite. 1. From the bed of magnetic iron ore of the Tilley-Foster mine, Putnam County, New York (Breidenbaugh, *Sill. Am. J.* [3], vi. 25). 2. Radio-fibrous actinolite, from Felling, near Gfühl in Austria. Sp. gr. = 2·99 (Egger, *Min. Mitth.* 1874, 243). 3. Fibrous dichromatic actinolite from Le Selle Monzoni. Sp. gr. = 2·71 (John, *Verh. geol. Reichsanst.* 1875, 304).

SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	MgO	CaO	K ^a O	Na ^a O	H ^a O	
57·44	1·13	—	4·33	0·15	22·59	13·29	trace	trace	1·52 =	100·45
56·88	1·36	0·48	3·26	trace	26·43	12·35	—	—	— =	100·76
53·82	1·28	1·53	11·54	trace	18·07	10·33	0·30	1·01	2·12 =	100

Anthophyllite. 1. From Star Rock, Concord, Delaware County, Pennsylvania. Sp. gr. 3·20 (A. R. Leeds, *Sill. Am. J.* [3], vi. 25). 2. From the spherical masses of mica at Hermannschlag in Moravia (Brezina, *Min. Mitth.* 1874, 247).

SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	MgO	CaO	K ^a O	Na ^a O	H ^a O	
55·12	0·55	—	8·20	0·32	31·18	0·75	1·01	1·55	2·21 =	100·90
57·39	2·04	0·42	6·53	—	29·08	0·69	—	—	2·56 =	98·71

Grammatite or Tremolite. Grammatite from the granular limestone of Chejnow, near Tabor, has been analysed by F. Farsky (*Verh. geol. Reichsanst.* 1876, 208):

SiO ^a	Al ^a O ^a	FeO	MgO	CaO	
59·74	1·85	0·34	25·47	12·71 =	100·11.

On the variety called *Hexagonite*, see p. 1030.

A hornblentic mineral, occurring—together with quartz, eudialyte, nephelin, and small quantities of magnetic iron ore, orthoclase and plagioclase—as a constituent of a rock in the island of Kikkertarsursurok, West Greenland, has been analysed by J. V. Janovsky (*Ber.* vi. 1230, 1453):

SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	MgO	CaO	K ^a O	Na ^a O	P ^a O ^a	Loss by ignition	
44·24	1·80	4·27	29·46	2·21	3·11	8·84	1·31	0·83	2·33	1·35 =	99·75
44·06	—	not determined	—	—	—	8·78	—	—	—	not determined	
44·27	not det.	—	29·33	—	3·03	8·82	—	—	—	—	

* Determined by difference.

A thin section showed the presence of enclosed apatite, so that the phosphoric acid, together with 2·76 CaO, must be reckoned as apatite, and there will then remain only 6·08 CaO to be reckoned as silicate.

Hornblende rocks. *Hornblende-Andesite*.—A specimen of this rock, from Tusnad on the Budös, near Kronstadt in Transylvania, has been analysed, together with some of its constituent minerals, by K. John (*Verh. geol. Reichsanst.* 1874, 242).

1. Analysis of the rock. 2. Felspar corresponding, after deduction of 4·73 per cent. orthoclase, with the formula Ab^2An . 3. Mica containing traces of MnO and $1^{20}O^3$. Sp. gr. = 2·967.

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	CaO	MgO	K ^a O	Na ^a O	Loss by ignition
1.	60·64	21·08	3·98	—	5·42	0·94	1·72	4·26	2·81 = 100·85
2.	59·79	25·33	trace	—	8·34	0·75	0·79	5·09	0·84 = 100·93
3.	40·77	15·59	26·55	0·78	0·86	5·89	5·07	1·40	2·32 = 99·23

An *augite-hornblende andesite* from Toplitia near György, St. Miklos, in Transylvania, likewise analysed by John (*ibid.* 120), was found to contain :

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	CaO	MgO	K ^a O	Na ^a O	Loss by ignition
	61·09	20·31	5·10	6·09	0·81	2·01	3·87	0·97 = 100·25.

Sp. gr. = 2·6545. The rock contains in a dense ground-mass, small felspars consisting partly of plagioclase, partly of sanidin. The microscope shows a large proportion of augite, somewhat less of hornblende and of magnetic iron ore.

C. Doelter (*Jahrb. f. Min.* 1874, 645) gives the following analysis of a compact hornblende andesite from the Pietra Mori in the mining district of Transylvania.

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	CaO	MgO	K ^a O	Na ^a O	Loss by ignition
	58·02	22·30	4·91	1·22	7·31	2·01	1·36	2·78	1·01 = 100·92.

The rock consists of a pitch-black ground-mass in which are imbedded shining crystals of felspar and needles of hornblende.

Hornblende-Gabbro.—This rock is found on the St. Louis river, near Duluth in Minnesota. In outward appearance it closely resembles a coarse-grained hypersthene rock, and consists of predominating plagioclase (labradorite), a little orthoclase, hornblende, diallagite, pegmatite, titanite, apatite, and extremely small quantities of copper-pyrites and epidote, together with a little quartz. The hornblende is mostly of a light or dark-green colour, owing to the presence of viridite; sometimes it is of a brown colour, and penetrated by fine dark parallel systems of lines, but a remarkable feature of this brown variety is the entire absence of 'cleavage-cracks.' The apatite occurs in thick short crystals. An analysis of this rock showed it to have the following composition, viz. :—

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	CaO	MgO	K ^a O	Na ^a O	H ^a O
	49·15	21·90	6·60	4·54	8·22	3·03	1·61	3·83	1·92 = 100·80

(Streng a. Kloos, *Jahrb. f. Min.* 1877, 113).

HORN-MERCURY. See MERCURY CHLORIDES.

HORNSTONE PORPHYRY. See PORPHYRY.

HORSE-RADISH. The fresh root of this plant, analysed by A. Hilger (*Landw. Vers. Stat.* xxii. 75), was found to contain 83·45 per cent. water. Dried at 100° it yielded 11·5 per cent. of ash, containing 72·52 per cent. of matter soluble in water containing carbonic acid, and 27·48 insoluble, including 2·5 per cent. carbon and 2·7 sand.

The soluble portion contained :—

CaO	1·19
MgO	0·89
Na ^a O	0·28
K ^a O	51·41
HCl	2·19
SO ^a	22·73
CO ^a	15·31

The insoluble part contained :—

CaO	35·38
MgO	11·92
P ^a O ^a	41·92
Fe ^a O ^a	3·47
CO ^a	7·23
SiO ^a	5·39

HUANTAJAYITE. A mineral found by Raymondi at Huantajaya in Southern Peru. It crystallises in cubes and octohedrons having the composition $AgCl_2ONaCl$ (F. Sandberger, *Jahrb. f. Min.* 1874, 174).

HUMIC ACID and **HUMUS.** P. Thénard (*Compt. rend.* lxxxiii. 375) prepares pure humic acid by dissolving the crude product in potash, precipitating with

a slight excess of hydrochloric or sulphuric acid, washing the precipitate well with water, and keeping the spongy mass for forty-eight hours at a temperature of -12° to -15° . As the mass thaws, the humic acid separates in the form of a dense precipitate which is to be further washed on a filter. Preparations thus obtained leave when burnt only very small quantities of potassium salt, and exhibit on analysis a constant composition agreeing with the formula $C^{24}H^{10}O^{10}$.

According to E. Simon (*L'Institut*, 1875, 133) pure humic acid absorbs nitrogen, which then enters into chemical combination with the other constituents. Melsens finds that the faculty of absorbing nitrogen is not possessed by all humous substances. Experiments by Simon, which, however, seem to require confirmation, point to the conclusion that humic acid renders ordinary calcium phosphate soluble, by replacing part of its phosphoric acid. Humic acid and ammonium humate do not diffuse through parchment-paper, whereas the compounds of humic acid with phosphoric acid diffuse through it readily.

Diazoxybenzoic acid, $C^{11}H^4N^2O^3$, a black substance obtained by the action of nascent hydrogen on dinitrobenzoic acid, appears to be related to the group of humous substances (p. 277).

HUMITE. *Chondrodite*.—Several varieties of this mineral are found on the vein of magnetic iron ore in the Tilley-Foster mine, Putnam County, New York. It occurs in small grains disseminated through the entire vein, and accumulates especially in the neighbourhood of clefts and in the clefts themselves; it is then imbedded in distinctly crystalline forms in white serpentine. The following are analyses: *a*, of a brown variety; sp. gr. = 3.2; *b*, of a red variety.

	SiO ²	MgO	FeO	F	Total (¹)	O (²)	Total (²)
<i>a</i> .	35.42	54.22	5.72	9.00	104.36	3.79	100.57
<i>b</i> .	35.42	51.88	9.73	5.38	102.41	2.26	100.15

A grey-brown variety, probably a variety of the red, likewise occurs, but the quantity of it that could be isolated was not sufficient for analysis (E. S. Breidenbaugh, *Sill. Am. J.* [3], vi. 212).

According to E. S. Dana (*ibid.* x. 89) the chondrodite crystals of the Tilley-Foster mine may be referred to the three types distinguished by Scacchi and vom Rath (i. 930; 2nd Suppl. 650). Two analyses, by G. W. Hawes, of very pure material belonging to the second type gave:

SiO ²	MgO	FeO	Al ² O ³	F	Sp. gr.
34.10	53.17	7.17	0.48	4.14 = 99.06	3.22
34.05	53.72	7.28	0.41	3.88 = 99.34	

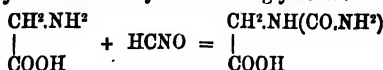
From the optical examination of the crystals (*ibid.* xi. 139), Dana concludes that those of the second type—if not the others—belong, not to the rhombic, but to the monoclinic system. According to C. Klein, the Vesuvian crystals of chondrodite are also monoclinic. Des Cloizeaux (*Phil. Mag.* [5], ii. 286), likewise on optical grounds, refers the crystals of the first type to the rhombic, those of the second and third types to the monoclinic system, and proposes to designate the first type as *humite*, the second as *chondrodite*, and the third as *clinohumite*.

On the relations of form and composition of Humite and Lievrite, see Websky (*Jahrb. f. Min.* 1876, 660; *Jahresb. f. Chem.* 1876, 1252; *Chem. Soc. J.* 1877, ii. 117).

Chondrodite from the dolomitic limestone of Svinetic, between Vodnan and Bavorov in the Bohemian forest, is described by R. Helmhacker (*Min. Mittheil.* 1873, 274).

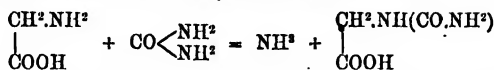
HYENIC ACID, $C^{25}H^{50}O^2$ (1st Suppl. 701). This acid appears to be contained, together with oleic acid, in the mixture of fatty acids produced by saponification of the compound ethers obtained from the grease of sheep's wool (Schulze a. Alrich, *Ber.* vii. 570).

HYDANTOIC ACID, $C^9H^4N^2O^3$ (1st Suppl. 702). *Glycoluric acid*.—This acid is formed: 1. By the action of cyanic acid on glycocine:



An aqueous solution of glycocine sulphate is heated with a slight excess of potassium cyanate, and the liquid, mixed with a considerable quantity of alcohol, is filtered from potassium sulphate, and left to evaporate (Wislicenus, *Liebigs Annalen*, clxv. 103).

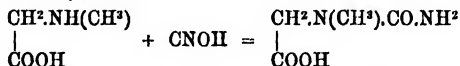
(¹) Including the O replaced by F. (²) Equivalent to the fluorine. (³) After deduction of the corresponding oxygen.

2. By heating glycocine with urea (Heintz, 1st *Suppl.* 702):

The formation of hydantoic acid in this manner is facilitated by boiling the two substances together with baryta-water; if an excess of urea is used, the conversion of the glycocine is almost complete (Baumann a. Hoppe-Seyler, *Ber.* vii. 34).

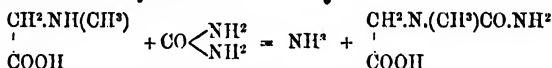
Methyl-hydantoic acid, $\text{C}^4\text{H}^5\text{N}^2\text{O}^3 = \text{C}^3\text{H}^4(\text{CH}_3)\text{N}^2\text{O}^3$. This acid, first obtained by O. Schultzen (*Ber.* v. 578) from the urine of a dog whose food was mixed with sarcosine (methyl-glycocine), has lately been produced synthetically from that compound by Baumann a. Hoppe-Seyler (*loc. cit.*) in the same manner as hydantoic acid from glycocine, viz.

1. By the action of cyanic acid:

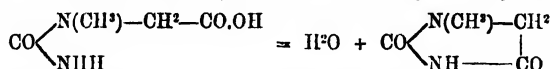


An aqueous solution of sarcosine is digested with potassium cyanate and an equal quantity of ammonium sulphate for two days in an air-bath at about 40° ; the liquid is then concentrated and freed from potassium sulphate by addition of alcohol; the alcoholic solution is supersaturated with baryta-water and evaporated; the baryta, after dilution of the liquid with water, is precipitated by carbonic acid; and the filtered liquid, after concentration to a small bulk, is mixed with a large quantity of strong alcohol. The resulting precipitate of barium methyl-hydantoate, which becomes quite hard after a while, is washed with alcohol, dissolved in water, and cautiously decomposed by dilute sulphuric acid; the solution is repeatedly shaken up with ether containing alcohol; the united extracts are distilled in a water-bath; and the remaining solution is evaporated over sulphuric acid.

2. By boiling sarcosine and urea with excess of baryta-water, or digesting the same mixture for two days at 40° :



Methyl-hydantoic acid crystallises in transparent plates, not very soluble in cold water or alcohol, but easily soluble in the same liquids when warm; also in ether containing water or alcohol; it has a strong acid reaction and pleasant sour taste. The dilute solution may be heated to boiling without decomposition; but when the concentrated solution is heated on the water-bath, the methyl-hydantoic acid is resolved into water and methyl-hydantoin or glycolyl-methyl-carbamide:



The crystals of methyl-hydantoic acid may, however, be heated to 100° for a short time without decomposition, but if the heating be continued, water is gradually given off. In this respect the crystallised acid is more stable than its concentrated solution. The same conversion of methyl-hydantoic acid into methyl-hydantoin takes place when the acid is boiled with carbonate of lead or carbonate of barium to form the corresponding methyl-hydantoates, only traces of the acid passing into solution. The barium and copper salts of methyl-hydantoic acid do not crystallise (Baumann a. Hoppe-Seyler).

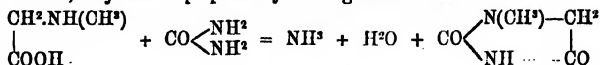
When moist silver oxide is added to a hot aqueous solution of methyl-hydantoic acid, and the liquid is filtered, the filtrate on cooling deposits a pulp of white shining laminae, the amount of silver in which agrees with the composition of silver-methyl-hydantoin, $\text{C}^4\text{H}^5\text{AgN}^2\text{O}^3$.

Methyl-hydantoic acid heated in a sealed tube at 130° – 140° with a hot-saturated solution of barium hydrate, yields ammonia, carbon dioxide, and a non-crystallisable syrup which has a sweetish taste, an acid reaction, and dissolves cupric hydrate abundantly. It forms a zinc salt which crystallises in large four-sided prisms, and contains a quantity of zinc indicating a mixture of methyl-di- and methyltri-glycolamic acids (E. Sulkowski, *Ber.* vii. 116).

The formation of methyl-hydantoic acid in the animal organism after the introduction of sarcosine does not appear to depend on the presence of previously formed urea. When sarcosine and urea were dissolved in a 2 per cent. solution of sodium bicarbonate, or in a 1 per cent. solution of the normal carbonate, and the liquid was

kopt for two days at a temperature of about 40° (blood-heat), no formation of methyl-hydantoic acid took place; neither was hydantoic acid obtained by proceeding in a similar manner with urea and glycocine. Moreover, hydantoic acid was not produced by passing carbon dioxide into a cooled solution of glycocine in strong aqueous ammonia, or when dry carbon dioxide and ammonia gases (which together form ammonium carbamate) were passed into a capacious flask containing glycocine hydrochloride. These experiments show that carbamic acid, when brought in contact with glycocine or sarcosine, has no tendency to unite with it and eliminate water; and they rather tend to support the view which ascribes the formation of urica or of methyl-hydantoic acid in the animal organism, to the direct addition of a cyanic acid residue to ammonia or sarcosine respectively (Baumann).

Methyl-hydantoin, formed as above-mentioned by dehydration of methyl-hydantoic acid, may also be prepared by melting sarcosine with urea:



It melts, according to Salkowski, at 154°–155°, i.e. at a temperature about 10° higher than the melting point originally assigned to it by Neubauer (1st Suppl. 703). Baumann found that a preparation which at first melted at 145°–146°, acquired, after repeated crystallisation, the higher melting point determined by Salkowski.

Phenyl-hydantoin, $\text{C}^6\text{H}_5\text{N}^2\text{O}^2 = \text{CO} \begin{array}{c} \text{N}(\text{C}^6\text{H}_5)-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{NH} \quad \text{CO} \end{array}$, is obtained, by fusing a

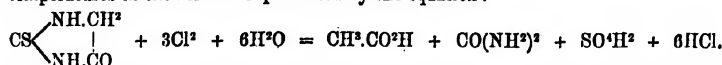
mixture of urea and phenyl-glycocine at 155°. It forms a crystalline mass of slender needles; melts at 191°; dissolves in water and in alcohol after prolonged boiling; but is only slightly soluble in cold alcohol, and still less in cold water. It dissolves in alkalis and is reprecipitated by acids. The ammoniacal solution gives white precipitates with silver nitrate and barium chloride, and does not dissolve freshly precipitated mercuric oxide or silver oxide. The aqueous solution does not exhibit the reactions just mentioned (P. Schwebel, *Ber.* x. 2045).

Tolyl-hydantoic acid, $\begin{array}{c} \text{CH}_3\text{N}(\text{C}^6\text{H}_5)\text{CO.NH}^2 \\ | \\ \text{COOH} \end{array}$, and **Tolyl-hydantoin**,

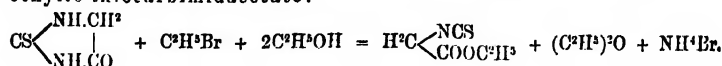
$\begin{array}{c} \text{CH}_3\text{N}(\text{C}^6\text{H}_5) \\ | \\ \text{CO} \quad \text{NH} \end{array} \text{CO}$, are obtained, together with other compounds, when urea and paratolyl-glycocine are fused together in equal numbers of molecules. Hot alcohol extracts from the fused product tolyl-hydantoic acid and monotolyl-carbamide, leaving tolyl-hydantoin and a crystalline substance (m. p. 174°) undissolved. On evaporating the alcoholic extract, tolyl-hydantoic acid is obtained as a white powder, insoluble in cold water and cold alcohol, and sparingly soluble in boiling alcohol. It decomposes at 200° without melting, and is precipitated from its solution in ammonia by acids. On adding hydrochloric acid to the mother-liquor from the tolyl-hydantoic acid, the monotolyl-carbamide separates out, and is deposited from a solution in hot alcohol in silvery needles, which are insoluble in water and ammonia, and are not attacked by acids or alkalis. It decomposes at 200°. Tolyl-hydantoin crystallises in colourless needles (m. p. 210°) insoluble in cold water, but soluble in alcohol (Schwebel, *Ber.* xi. 1128).

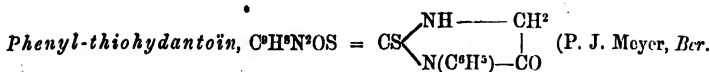
Thiohydantoin or **Glycolyl-thiocarbamide**, $\text{C}^2\text{H}^2\text{N}^2\text{OS} = \text{CS} \begin{array}{c} \text{NH}-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{NH}-\text{CO} \end{array}$

(p. 400). This compound, unlike thiocarbamide itself (p. 395), does not unite directly with chlorine and bromine, but is decomposed by chlorine in presence of water at low temperatures in the manner represented by the equation:



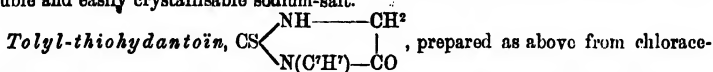
Bromine acts in a similar manner at ordinary temperatures, but the carbamide at the moment of its formation is resolved into CO_2 and NH_3 . Thiohydantoin, heated to 130°–140° with ethyl bromide and alcohol, yields, not an additive compound, but ethylic thiocarbimidacetate:





x. 1965).—This compound is formed when chloracetamide and thiocarbamide dissolved in alcohol are heated together on the water-bath. Thiohydantoïn then crystallises out first, and from the filtrate water throws down phenyl-thiohydantoïn. The same compound is formed when phenyl-thiocarbamide and ethyl-monochloracetate are heated together in alcoholic solution, and the product, after being made alkaline, is treated as above.

Phenyl-thiohydantoïn forms small shining slightly yellow needles or prisms, which melt at 108° ; it is nearly insoluble in water, sparingly soluble in cold, easily in hot alcohol, also in ether and in acids. With caustic soda-solution it forms a very soluble and easily crystallisable sodium-salt.



toluide and thiocarbamide, crystallises in small shining needles or prisms melting at 183° (Meyer, *loc. cit.*)

A second phenyl-thiohydantoïn appears to be formed on fusing together phenyl-glycocine and thiocarbamide.

Thiohydantoic or Thiocarbamidacetic acid, $C^6H^5N^2O^2S$, is formed by the action of thiocarbamide, aided by heat, on a solution of the monochloracetate of sodium or ammonium. It is a white crystalline powder composed of microscopic four or six-sided tablets and prisms, soluble in hot water, also in alkalis and acids, otherwise insoluble. It decomposes when heated. The aqueous solution is quite neutral, and does not form a precipitate with silver nitrate; but, on adding a small quantity of ammonia, yellowish flocks are thrown down. The acid appears to form salts, but they are very unstable. By alkalis, even sodium carbonate, and by acids, it is easily converted into thiohydantoïn, and the same change takes place partially even on recrystallising the acid (R. Maly, *Wien Akad. Ber.* [2 Abth.], lxxv. 712).

HYDRASTIS. The root of *Hydrastis canadensis* is known to contain two alkaloids, viz. hydrastine and berberine (iii. 178; 2nd Suppl. 655), and a third has been detected in it by A. E. Hale (*Pharm. J. Trans.* [3], iv. 105). When ammonia is added to the aqueous extract of the plant from which the hydrochloride of berberine has already been separated, as long as a precipitate is thereby produced, and the solution of this precipitate in alcohol is left to evaporate, a crystalline substance is obtained apparently coloured by a yellow powder. If, on the other hand, the aqueous filtrate be merely neutralised with ammonia, and the resulting precipitate dissolved in alcohol, the solution thus obtained deposits colourless crystals of hydrastine. On further addition of ammonia, however, a new precipitate is formed of darker colour than berberine, neutral in alcoholic solution to test-paper, and differing from berberine also in other respects, being less soluble in cold nitric acid, and forming a solution which turns red when warmed. Its solution in hydrochloric acid does not deposit crystals till it is nearly cold. The new alkaloid dissolves in hot sulphuric acid with red-brown colour; it is more soluble than berberine in water and in cold potash solution, and forms, with a solution of mercuric iodide in potassium iodide, a slight yellow precipitate.

The existence of this third alkaloid in *Hydrastis canadensis* is confirmed by J. C. Burt (*Pharm. J. Trans.* [3], vi. 467), who finds that the sulphate crystallises in radial tufts of prismatic needles, and that the hydrochloride gives precipitates of yellow to reddish- or brownish-yellow colour.

The alkaloid, distilled in alkaline solution with potassium permanganate, gives off traces of ammonia, and therefore probably contains nitrogen.

HYDRATES. Church (*Chem. News*, xxxiii. 203) proposes to classify hydrates occurring in nature according to the conditions under which their combined water is retained: viz. (1) *Cryohydrates*, which retain their water only at low temperatures. (2) *Hygrohydrates*, which retain it only in a moist atmosphere. (3) *Barohydrates*, which give it up under diminished pressure. An example of a hygro- and barohydrate is afforded by the native uranio-calcic phosphate called *autunite*, which in the natural state is a hygrohydrate containing 10 mol. H^2O , 5 of which it gives off in dry air, being thereby converted into a barohydrate, which gives off 3 mol. H^2O in a vacuum.

On *Cryohydrates*, see also pp. 1005–1009.

On the Heat of Formation of Crystalline Hydrates, see HEAT, p. 982; on their Decomposition by Heat, pp. 1012–1016.

HYDRAZINES. The name hydrazine is given to the group N^2H^4 or H^2N-NH^2 , i.e. ammonia in which 1 atom of hydrogen is replaced by amidogen. This compound is not actually known, but several of its derivatives have been obtained in which one or more of the hydrogen-atoms are replaced by radicles, alcoholic or acid. The hydrazines containing only alcohol-radicles are all of basic character, and, like the amines, are designated as primary or secondary, according to the number of hydrogen atoms thus replaced. Tertiary hydrazines containing only alcohol-radicles have not yet been obtained. Each hydrazine contains 1 at. N. and 1 at. H. more than the corresponding amine: viz.

Ethyl-amine, $C^2H^5.NH^2$

Ethyl-hydrazine, $C^2H^5.N^2H^3$

Diethyl-amine, $C^2H^5.NH.C^2H^5$

Diethyl-hydrazine, $C^2H^5.N^2H^3.C^2H^5$

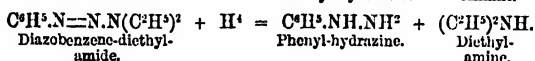
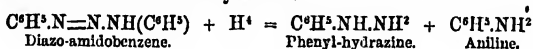
A. PRIMARY AROMATIC HYDRAZINES.

These bases, represented by the general formula

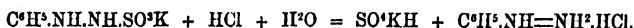


in which R stands for phenyl and its homologues, are produced by the action of reducing agents on diazobenzene-compounds and on aromatic nitrosamines.

Phenyl-hydrazine, $C^6H^5.N^2H^3$ (E. Fischer, *Deut. Chem. Ges. Ber.* viii. 589, 1005, 1587, 1641; ix. 111, 454, 880; *Liebigs Annalen*, xc. 67-145). *Formation and Preparation.*—1. By the action of zinc and acetic acid on diazoamidobenzene and diazobenzene-diethylamide:



2. By adding diazobenzene nitrate, $C^6H^5.N=N.NO^3$, to a cold solution of hydrogen-potassium sulphite, whereby it is converted into yellow crystals of potassium diazobenzene-sulphonate, $C^6H^5.N=N.SO^3K$; and heating this salt on the water-bath with excess of hydrogen-potassium sulphite, or with zinc-dust and hydrochloric acid, whereby it is converted into colourless phenylhydrazinesulphonate, $C^6H^5.NH.NH.SO^3K$, which, when heated with hydrochloric acid, yields the hydrochloride of phenylhydrazine:



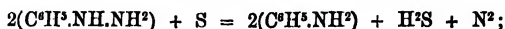
3. By heating the dry white phenylhydrazinesulphonate (50 pts.) with benzoyl-chloride (70 pts.), and chloroform (80-90 pts.) as long as hydrochloric acid continues to escape, and heating the resulting dibenzoylphenyl-hydrazine, $C^6H^5.N^2H(C^7H^5O)^2$, to 100° with hydrochloric acid of sp. gr. 1.19, whereupon it splits up completely into benzoic acid and phenyl-hydrazine.

4. Commercial potassium nitrite (25 pts.) is gradually added to a cooled mixture of 20 pts. aniline, 80 water, and 50 hydrochloric acid (sp. gr. 1.19), and this mixture is slowly poured into a solution of commercial sodium sulphite in excess. The liquid is then nearly neutralised with hydrochloric acid, treated on the water-bath with zinc-dust till it becomes colourless, and finally concentrated, with addition of small quantities of hydrochloric acid, till the hydrochloride of phenyl-hydrazine separates out. This reaction is recommended by Fischer as affording an easy method of preparing hydrazine-compounds.

Phenyl-hydrazine is, at ordinary temperatures, a nearly colourless oil, of sp. gr. 1.091 at 21° , and boiling at $233^\circ-234^\circ$; on exposure to cold it solidifies to a crystalline mass of shining tables, which melt at 23° . It is somewhat soluble in hot water, but almost insoluble in concentrated solutions of the alkalis: it is miscible in all proportions with alcohol, ether, benzene, and chloroform. In presence of reducing agents it is exceedingly stable, but it is very readily decomposed by oxidants: it reduces Fehling's solution even when in cold dilute solution, and this reaction, by reason of its delicacy, is recommended for the discrimination of all primary hydrazines, and indirectly of diazo-compounds. It is a monacid base, yielding well-defined crystalline salts. The *hydrochloride*, $C^6H^5.N^2H^3.HCl$, is a colourless salt crystallising in shining plates, which may be sublimed unchanged. It is precipitated from its aqueous solution by concentrated hydrochloric acid. The *sulphate*, $(C^6H^5.N^2H^3)^2H^2SO^4$, and *nitrate*, $C^6H^5.N^2H^3.OH.C^6H^5(NO^3)^3$, crystallises in slender yellow needles, the *oxalate*, $(C^6H^5.N^2H^3)^2H^2C^2O^4$, in colourless plates.

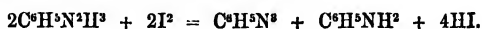
Reactions.—(1). With Sulphur. Phenyl-hydrazine heated with sulphur is decomposed—the action beginning at 80°—with formation of nitrogen, ammonia, hydrogen sulphide, benzene, aniline, thiophenol, phenyl sulphide, and phenyl disulphide.

The action of sulphur upon the hydrazines appears, therefore, for the most part, to be limited to their nitrogenous group, and is similar to the decomposition of these bases by oxidation in their alkaline solution. The formation of aniline, which occurs to the extent of 30 per cent. of the phenyl-hydrazine employed, is explained by the equation:



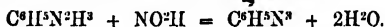
that of benzene and the various sulphur-derivatives enumerated resembles the ordinary decomposition of the diazo-compounds.

2. With Halogens. Aqueous emulsions of phenyl-hydrazine, treated alternately with iodine and potassium hydrate, take up iodine and form diazo-benzenimide, aniline, and iodanilines, probably according to the equation:



Chlorine and bromine act much more energetically, decomposing the nitrogen-group of the hydrazine.

3. With Nitrous acid and Nitrites. When gaseous nitrogen trioxide is passed into an aqueous or ethereal solution of phenyl-hydrazine, diazobenzenimide, $C^6H^5.N^2$, is formed, together with dark-coloured resinous products:



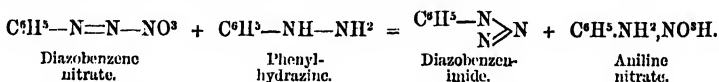
When, on the other hand, sodium nitrite is added in excess to a cooled solution of phenyl-hydrazine hydrochloride in 10 pts. of water, the liquid becomes turbid, gives off the intoxicating odour of diazobenzenimide, and after a while deposits yellow crystalline flocks of phenyl-nitrosohydrazine:



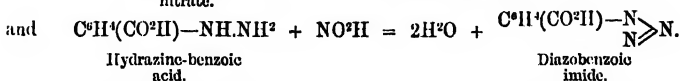
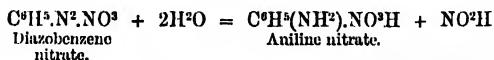
This reaction is very characteristic of the primary hydrazines.

4. With Diazobenzene. The action of diazobenzene-salts on the aromatic hydrazines does not give rise to compounds analogous to the diazo-amido-compounds, which are formed by the action of diazobenzene-salts on amines (*e.g.* diazo-amido-benzene and diazo-dimethylamide from aniline and dimethylamine respectively), but proceeds in a different manner, which is as characteristic of the primary hydrazines as the action of nitrous acid.

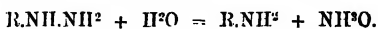
When pure nitrate or sulphate of diazobenzene is added to a cold aqueous solution of phenyl-hydrazine hydrochloride, the liquid soon becomes turbid, from separation of diazobenzenimide, while a salt of aniline remains dissolved:



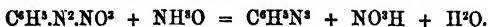
This reaction is analogous to that which Griess observed with diazobenzene nitrate and hydrodiazobenzoic or hydrazine-benzoic acid, or with diazobenzoic nitrate and phenyl-hydrazine, whereby diazobenzoic imide, $C^6H^4(CO^2H)-\overset{N}{\underset{N}{\parallel}}N$, and aniline nitrate, or diazobenzenimide and amidobenzoic nitrate, are produced (p. 276). The formation of the diazo-benzoic imide is attributed by Fischer to a regeneration of aniline and nitrous acid, consequent on the assumption of 2 mol. H^2O by the diazobenzene, and to the action of the nitrous acid thus formed on hydrazine-benzoic acid, thus:



To explain the simultaneous formation of amidobenzoic acid and diazobenzenimide, it is necessary to suppose that the hydrazine-group is split up, and that nitrogen is transferred to the diazobenzene. This result may likewise be brought about by assumption of water, the hydrazine being resolved into the corresponding amine and hydroxylamine:

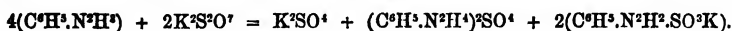


The last reaction has not, indeed, been effected in the simple form here represented; but there are sufficient grounds for supposing it to take place, especially in the secondary hydrazines. The hydroxylamine thus formed will unite with the diazobenzene, forming water and diazobenzenimide:



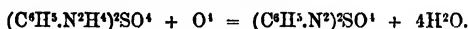
That such is actually the case may be shown by pouring a mixture of the cold aqueous solutions of diazobenzene sulphate and hydroxylamine hydrochloride into a cold dilute solution of sodium carbonate, whereupon diazobenzenimide separates out nearly in the quantity required by theory. Further evidence in support of the explanation just given is that the secondary base, methylphenyl-hydrazine, is decomposed in a similar manner by diazobenzene, yielding diazobenzenimide and methylaniline.

5. *Reconversion of Hydrazines into Diazo-compounds*.—This transformation may be effected through the medium either of the sulphonates or of the ordinary salts (chlorides, sulphates, &c.) of the hydrazines, most readily, however, with the former. The hydrazine sulphonate is prepared by heating 2 mol. of the base with 1 mol. potassium pyrosulphate, whereby a pasty mixture of potassium sulphate, phenyl-hydrazine sulphonate, and phenyl-hydrazine sulphonate is formed, which soon solidifies:



To isolate the last salt, the melt is dissolved in hot water, and the greater part of the sulphuric acid removed by barium carbonate, the phenyl-hydrazine which was combined with that acid then separating for the most part as an oil; and on adding strong potash-ley to the hot filtered liquid, the hydrazine-sulphonate is deposited in a mass of crystals which may be obtained pure by one recrystallisation from hot water. The hydrazine-sulphonate may then be converted into the yellow diazosulphonate, $\text{C}^6\text{H}^5\text{.N}^2\text{.SO}^2\text{K}$, by oxidation with mercuric oxide or potassium dichromate.

The conversion of the sulphate, chloride, &c., of the hydrazine to a diazo-compound by oxidation is less easy and requires special precautions to prevent the occurrence of secondary reactions. The best way of proceeding is to add the aqueous solution of the hydrazine salt gradually, and with continual agitation, to water holding in suspension an excess of mercuric oxide. The reaction then takes place to a great extent in the manner represented by the equation:

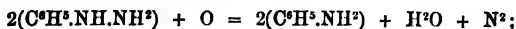


The formation of phenyl-hydrazine from diazobenzene, and its reconversion into the latter by the reactions above described, are more readily explained by Kekulé's formula of the diazobenzene-compounds, viz. R-N=N-R' , containing only trivalent

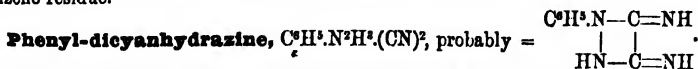
nitrogen, than by Strecker's formula $\begin{array}{c} \text{R}-\text{N}-\text{R} \\ ||| \\ \text{N} \end{array}$, in which one of the N-atoms is quin-

ivalent (p. 636). For all these reactions, indeed, Strecker's formula would require intra-molecular transpositions, and the conversion of quinquivalent into trivalent nitrogen by addition, and of trivalent into quinquivalent nitrogen by abstraction of hydrogen, which does not appear very probable.

4. *Oxidation of Phenyl-hydrazine in Alkaline Solution*.—The oxidation of phenyl-hydrazine, in presence of mineral acids, gives rise, as already observed, to diazobenzene or its transformation-product, diazobenzenimide, and is not attended with evolution of gas; in alkaline solutions, on the other hand, Fehling's solution for example, nitrogen is evolved, and the products formed are aniline and benzene. The formation of aniline is explained by the equation:



that of benzene is probably due to the decomposition of a diazo-compound, with entire evolution of its nitrogen in the form of gas, and the entrance of its hydrogen into the benzene residue.



When cyanogen gas is passed into an emulsion of 1 pt. phenyl-hydrazine and 10 pts. water, yellowish-red crystals are obtained which, after washing with water, may be purified by recrystallisation from alcohol, with addition of animal charcoal. They are still however yellow after this treatment, and it is only by repeated solution in ether and precipitation with ligroin, which is attended with great loss of substance, that they can be obtained nearly white. They consist of phenyl-dicyanhydrazine, which,

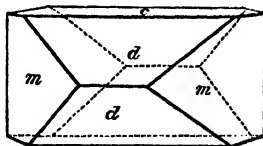
from the analogy of its mode of formation to that of di-cyananiline, may perhaps be represented by the constitutional formula above given.

Phenyl-diethanhydrazine dissolves easily in alcohol, and in ether, sparingly in water and in ligroin. From hot water it crystallises in jagged feathery groups which unite into laminae; from benzene, chloroform, or an ethereal solution mixed with ligroin, it separates in crystals which, according to Arzruni, are monoclinic, with strongly curved faces. It turns brown at 160°, and melts with decomposition at a slightly higher temperature. It dissolves in dilute hydrochloric acid, and is separated from the solution by neutralisation with soda. Its cold aqueous solution gives with Fehling's solution a dingy green precipitate and a blue-green coloration. It reduces ammoniacal silver solutions. Its alkaline solution, when exposed to the air, absorbs oxygen and turns brown. The cyanide is not much affected by acids, but when heated to 150° for several hours with water, it is converted into white needle-shaped crystals. Its solution in sulphuric acid gives a white flocculent precipitate with potassium nitrite.

Phenyl-azonium Compounds. Azonium compounds are bodies related to the hydrazines in the same manner as the ammonium compounds to the amines, and produced in like manner by the combination of hydrazines with the bromides, chlorides, hydroxides, &c., of alcohol-radicles.

Phenyl-diethyl-azonium Bromide, $C^6H^5.N^2H^2(C^2H^5).C^2H^5Br$.—When phenyl-hydrazine and ethyl bromide are mixed together in molecular proportions, reaction begins at ordinary temperatures, and must be moderated at first by immersing the vessel in cold water, but to complete it the mixture must be gently heated in a reflux apparatus. With 1 mol. of the base to 1½ mol. ethyl bromide (a slight excess of the latter being advantageous), the liquid solidifies completely to a magma of white slender needles, which may be freed from the slight excess of ethyl bromide by warming on the water-bath. This product dissolves completely in water, and the solution, after being freed from volatile bases by extraction with ether, yields phenyl-diethylazonium bromide as a precipitate composed of white slender needles; and by passing these between filter paper and recrystallising from boiling alcohol, the compound is obtained in short transparent prisms, or by slow evaporation of the alcoholic solution in shining splendidly developed rhombic prisms, exhibiting the combination ∞P , $\bar{P}\infty$, $0P$ (fig. 5), mostly elongated in the direction of the macrodiagonal. The faces ∞P and $\bar{P}\infty$ are often equally developed, while $0P$ is narrow, and striated parallel to its combination edge with $\bar{P}\infty$. Axes $a : b : c = 0.8219 : 1 : 0.8265$. The plane of the optic axes is parallel to the brachypinacoid, and the first median line coincides with the axis c . Dispersion of the optic axes $\rho < \nu$. Double refraction positive, strong.

FIG. 5.

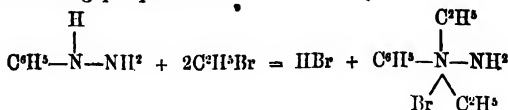


$c = 0P$, $d = \bar{P}\infty$, $m = \infty P$.

Phenyl-diethylazonium bromide dissolves very easily in water, very sparingly in strong alkalis, and is insoluble in ether. At 180° it begins to turn brown, and at 193° it decomposes rapidly, giving off gas and yielding a yellow oily distillate, while a half-charred mass remains in the retort.

In its chemical relations, this bromide exhibits the characters of an ammonium compound; it is not altered by alkalis, but is easily debrominated by the oxide and salts of silver, yielding with the former a hydroxide easily soluble in water and having an alkaline reaction. By agitating its aqueous solution with recently precipitated silver chloride, it is quickly converted into the chloride, which is likewise easily soluble in water, and unites with platonic chloride, forming brown-yellow crystals of the platinochloride, $[C^6H^5N^2H^2(C^2H^5)_2Cl]^+PtCl_4^-$.

The constitution of these azonium-compounds seems at first sight to throw some doubt on the universality of Hofmann's conclusion that the formation of compounds of the ammonium-type from those of the ammonia-type takes place only after the typical hydrogen of the latter has been completely replaced by alcohol-radicles. The discrepancy may, however, be removed by supposing that in the action of ethyl bromide on the hydrazine base, the hydrogen of the NH -group is first replaced by ethyl, and the ethyl bromide added on to the ethylimidogen-group thus formed, the nitrogen then becoming quinquivalent:



The correctness of this view is indeed demonstrated by the fact that phenyl-diethylazonium bromide is likewise produced by heating phenyl-ethyl-hydrazine, $C^6H^5.N(C^2H^5).NH^2$, with ethyl bromide. It must therefore be inferred that the formation of a compound of the ammonium-type, while it indicates the presence of a tertiary amine group, does not afford any criterion as to the number of hydrogen-atoms which may be present therein in combination with nitrogen, but that such a compound may contain imide- or amide-groups yet intact.

Derivatives of Phenyl-hydrazine containing Acid Radicles.

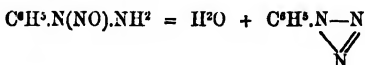
1. **Phenyl-nitrosohydrazine**, $C^6H^5-N(NO)-NH^2$. The formation of this compound by the action of sodium nitrite on phenyl-hydrazine hydrochloride has been already noticed (p. 1049). The yellow-brown flocks first deposited may be purified by washing with water, pressure between filter-paper, solution in warm ether, and precipitation with ligroin, which throws down the compound in yellow laminae.

Phenyl-nitrosohydrazine, like other nitroso-bases, exhibits Liebermann's colour-reactions with phenol and sulphuric acid (2nd Suppl. 901); the blue colour with potash does not however appear immediately, but only after agitation with air, because the colouring matter, at the moment of its formation, is reduced by the hydrazine-group—just as Liebermann observed that it was reduced by zinc-dust—and the colour does not appear till oxidation has taken place by the action of the air. Similar reactions are exhibited by most nitroso-derivatives of the hydrazine-bases.

Phenyl-nitroso-hydrazine may be exposed to the air without alteration for several days, especially in the state of fine powder and in thin layers; but when kept in closed vessels, it decomposes very quickly, at summer temperature even in a few hours, and is converted into a dark brown strong-smelling liquid. Its vapour is very poisonous, acting like that of amyl nitrite, but much more strongly, the inhalation even of a small quantity producing determination of blood to the head and violent headache.

Phenyl-nitroso-hydrazine treated with zinc and sulphuric acid, or with zinc-dust and acetic acid, yields considerable quantities of aniline. This reduction, differing as it does from that observed by Baeyer & Caro (p. 205) in the case of dimethyl-nitrosaniline, in which the NO-group is contained within the benzene-nucleus, shows that in phenyl-nitroso-hydrazine, the NO is situated in the hydrazine group N^2H^3 , and as moreover Heintz has shown (*Liebig's Annalen*, cxxxviii, 316) that in the ordinary amine-bases, the formation of a nitrosamine takes place only when imide-groups are present, it may be inferred as highly probable that the same is the case with hydrazines, and that consequently in the compound under consideration the NO is situated in the NH^2 -group, so that its constitutional formula is $C^6H^5.N(NO).NH^2$. This conclusion is strongly corroborated by the fact that the secondary aromatic hydrazines, to be described further on, in which the hydrogen of the NH^2 -group is replaced by an alcohol-radicle, are decomposed by nitrous acid in a totally different way.

Phenyl-nitroso-hydrazine, gently heated with a dilute alkali, is completely resolved into water and diazobenzenimide, $C^6H^5N^3$:

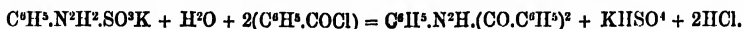


2. **Phenyl-hydrazides**. Two of the hydrogen-atoms in phenyl-hydrazine are easily replaced by acid organic radicles; for the third the substitution has not yet been effected. The resulting compounds exhibit, in general, the characters of ordinary amides. The first acid radicle which enters appears always to take the place of a hydrogen-atom in the NH^2 -group of the hydrazine, as is proved by the direct conversion of some of the resulting compounds into azo- and diazo-compounds; the position of the second is as yet undecided.

Monobenzoyl-phenyl-hydrazide, $C^6H^5.NH.NH(COC^6H^5)$, is formed by gradually adding benzoyl chloride (1 mol.) to a solution of phenyl-hydrazine (2 mol.) in 5 pts. of ether. The crystals which separate are freed from phenyl-hydrazine hydrochloride by treatment with hot water, and then recrystallised from alcohol. The compound dissolves sparingly in hot water and in ether, freely in hot alcohol, acetone, and chloroform, and crystallises from all these solutions in slender white prisms. It melts at 168° , and decomposes at higher temperatures; dissolves without alteration in potash-ley, but is decomposed by hydrochloric acid at 100° into phenyl-hydrazine and benzoic acid. On adding mercuric oxide to its solution in chloroform, the oxide is reduced and the liquid acquires a dark red colour, from formation of

benzoyl-diazobenzene, $\text{C}_6\text{H}_5\text{—N=N—CO}\cdot\text{C}_6\text{H}_5$. This latter compound is a dark red oil which dissolves easily in alcohol, ether, and chloroform; detonates slightly when heated; is completely decomposed by boiling with water or with acids; is not further oxidised by Fehling's solution; and is reconverted by zinc and acetic acid into benzoyl-phenyl-hydrazide.

Dibenzoyl-phenyl-hydrazide, $\text{C}_6\text{H}_5\cdot\text{N}_2\text{H}(\text{CO}\cdot\text{C}_6\text{H}_5)_2$, may be obtained by the action of benzoyl chloride on monobenzoyl-phenyl-hydrazide, but is more easily prepared by that of benzoyl chloride on potassium phenyl-hydrazine-sulphonate:



It is very slightly soluble in water, moderately in hot alcohol; by dilute alkalis at the boiling heat, it is taken up slowly but in considerable quantity, and separated unaltered by acids. In alcoholic solution it immediately reduces ammoniacal silver nitrate. Heated in a sealed tube with fuming hydrochloric acid, it is completely resolved into phenyl-hydrazine and benzoic acid. It melts at $177^\circ\text{--}178^\circ$, and decomposes at a higher temperature, yielding a distillate containing benzoic acid, benzoic aldehyde, and benzanilide, and a resinous residue which ultimately carbonises.

Acetyl-phenyl-hydrazide, $\text{C}_6\text{H}_5\cdot\text{N}_2\text{H}_2\cdot\text{CO}\cdot\text{CH}_3$, is produced, with great rise of temperature, on mixing acetic anhydride (1 mol.) with phenyl-hydrazine (2 mol.), the liquid turning brown and solidifying slowly to a slightly coloured crystalline mass. This is dissolved in hot water, and the solution is filtered from a small quantity of resinous products and left to cool, whereupon it deposits the acetyl-phenyl-hydrazide in nearly colourless laminae, which may be purified by crystallisation from dilute alcohol. The compound may also be prepared by boiling phenyl-hydrazine for several hours with three times its weight of glacial acetic acid, the excess of the latter being removed by distillation at 160° , and the residue purified as above.

Acetyl-phenyl-hydrazide is slightly soluble in cold water and ether, easily in hot water, alcohol, chloroform, and benzene, and crystallises from most of these solutions in six-sided prisms often shortened to thin plates, and having a bright silky lustre. It melts at $128\cdot5^\circ$, and distils at a higher temperature, for the most part without decomposition; is resolved by boiling with strong acids into acetic acid and phenyl-hydrazine. Its aqueous solution instantly reduces Fehling's solution when gently heated therewith. Dissolved in dilute sulphuric acid and treated with sodium nitrite, it yields an unstable nitroso-derivative. By prolonged boiling with acetic anhydride, it is converted into a syrupy mass, probably containing a diacetyl-derivative. Acetyl-phenyl-hydrazide, oxidised in chloroform-solution by mercuric oxide, is decomposed like the benzoyl-compound, yielding a dark red oil, probably consisting of acetyl-diazobenzene, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{CO}\cdot\text{CH}_3$.

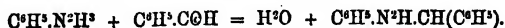
Oxalyl-diphenyl-hydrazide, $(\text{C}_6\text{H}_5\cdot\text{N}_2\text{H}_2)_2\text{C}\cdot\text{O}_2$.—This compound, analogous in composition to oxamide, is produced in a similar manner by heating a mixture of 1 mol. ethyl oxalate and 2 mol. phenyl-hydrazine to 110° , alcohol being given off with ebullition, and the solution solidifying to a faintly yellow laminar crystalline mass. It begins to soften at 260° , and melts completely at $277^\circ\text{--}278^\circ$; at a higher temperature it distils for the most part unaltered, and the distillate on cooling immediately solidifies in the crystalline form. It is but slightly soluble in most solvents; is dissolved by strong sulphuric acid in the cold with red-violet colour, and without further alteration, and is completely decomposed on boiling.

Derivatives of Phenyl-hydrazine containing Aldehyde-radicles.

Phenyl-hydrazine and the aldehydes unite, with elimination of water, to form in nearly all cases well crystallised, indifferent bodies, containing the residues of 1 mol. of each reagent: in this respect they differ from the otherwise similar derivatives of the ordinary amine bases. Some of the compounds thus formed are very stable, while others are completely decomposed by boiling with water, or by prolonged exposure to the air. By heating with fuming hydrochloric acid, they are all completely resolved into phenyl-hydrazine and the corresponding aldehyde.

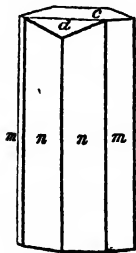
Benzylidene-phenyl-hydrazide, $\text{C}_6\text{H}_5\cdot\text{N}_2\text{N} = \text{C}_6\text{H}_5\text{—NH—N=CH—C}_6\text{H}_5$. On mixing phenyl-hydrazine with bitter almond oil, a violent reaction takes place, the mixture becoming turbid from separation of water, and solidifying on cooling to a slightly coloured crystalline mass. In preparing large quantities it is advisable to moderate the violence of the reaction by adding about 2 vols. of alcohol, and to mix the base and the aldehyde in equal numbers of molecules. The crystalline mass

which separates is filtered off and purified by recrystallisation from absolute alcohol. The reaction takes place according to the equation :



Benzylidene-phenyl-hydrazide is quite colourless when pure, but quickly becomes rose-red when exposed to the air. It melts at $152\cdot5^\circ$; distils without decomposition; dissolves easily in hot alcohol, acetone, and benzene, sparingly in ether. By slow evaporation of a dilute alcoholic solution, it may be obtained in well-defined elongated prismatic crystals (fig. 6) of rose-red colour. They belong to the monoclinic system. Axes $a : b : c = 0\cdot853 : 1 : 0\cdot670$. Angle $ac = 87^\circ 40' 30''$. Observed combination $8\text{P} : \infty\text{P}2 : 0\text{P} : -\text{P}\infty$. Angle $\infty\text{P} : 0\text{P} = 88^\circ 14'$; $\infty\text{P} : \infty\text{P}2 = 47^\circ 30'$. Plane of the optic axes coincident with the plane of symmetry.

FIG. 6.



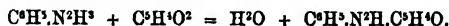
$m = \infty\text{P}$; $n = \infty\text{P}2$;
 $c = 0\text{P}$; $d = -\text{P}\infty$.

Benzylidene-phenyl-hydrazide does not reduce Fehling's solution, even with the aid of heat. By prolonged boiling with fuming hydrochloric acid, or better, with sulphuric acid of 30 per cent., it is slowly resolved into phenyl-hydrazine and benzaldehyde.

Ethylidene-phenyl-hydrazide, $\text{C}^6\text{H}^5\text{.N}^2\text{H.CH}_2\text{CH}_3$, is obtained by adding to an ethereal solution of phenyl-hydrazine rather more than an equivalent quantity of recently distilled acetaldehyde, till the mixture no longer reduces Fehling's solution. When the oily residue left on evaporation of the ether is stirred up with cold water, it gradually solidifies to a crystalline mass, which may be freed from colouring matters and obtained pure by repeated crystallisation from ligroin. This compound dissolves easily in ether and in alcohol, deliquesces slowly in the air to a red-brown liquid, and is resolved by boiling with water or dilute acids into aldehyde and phenyl-hydrazine.

A product essentially different from the above is obtained when the mixture of phenyl-hydrazine and aldehyde is directly heated with strong hydrochloric acid. The solution then becomes dark green, and, on addition of water or potash-ley, deposits a granulo-crystalline mass of complex composition. It exhibits weak basic properties, and dissolves in strong acids, but is separated therefrom even by water. It appears to be a hydrazine-derivative produced by further aldehyde-condensation, probably analogous to the bases which H. Schiff obtained in a similar manner from aniline.

Phenyl-furfurazide, $\text{C}^6\text{H}^5\text{.N}^2\text{H.C}^6\text{H}^4\text{O}$.—When phenylhydrazine and furfural are mixed in molecular proportions, the liquid becomes very hot, and slowly solidifies on cooling to a yellow crystalline mass, which may be purified by repeated solution in ether, drying with calcium chloride, and precipitation with ligroin. It then crystallises in faintly yellow laminae; melts at 96° ; decomposes at a higher temperature; dissolves easily in alcohol and ether, very sparingly in ligroin; and is resolved by boiling with hydrochloric acid into phenyl-hydrazine and furfural. Its formation is represented by the equation :



Phenyl-carbazides.

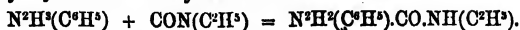
Carbazides are compounds derived from carbamides or ureas by substitution of one or two hydrazine groups, N^2H^3 , for NH^2 -groups. Those in which both the NH^2 -groups are thus replaced are called simply carbazides; those in which only one NH^2 -group is replaced are called semi-carbazides, thus:

Phenyl-carbamide	$\text{NH}^2\text{.CO.NH(C}^6\text{H}^5\text{)}$
Phenyl-semicarbazide	$\text{NH}^2\text{.CO.N}^2\text{H(C}^6\text{H}^5\text{)}$
Phenyl-carbazide	$\text{N}^2\text{H}^3\text{.CO.N}^2\text{H(C}^6\text{H}^5\text{)}$
Diphenyl-carbazide	$(\text{C}^6\text{H}^5)\text{N}^2\text{H}^3\text{.CO.N}^2\text{H(C}^6\text{H}^5\text{)}$

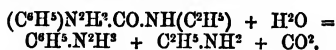
There are also carbazic acids related in like manner to the carbamic acids, e.g. *phenyl-carbazic acid*, $\text{C}^6\text{H}^5\text{.N}^2\text{H}^3\text{.CO.OH}$; and thiocarbazides, thiocarbazic acids, &c. analogous in constitution to the preceding, but containing sulphur in place of oxygen.

Carbazides are formed from hydrazines by reactions precisely analogous to those by which carbamides or ureas are formed from amines; but they differ considerably from carbamides in many of their reactions, the presence of the hydrazine-group exerting a modifying influence, which is especially conspicuous in the action of nitrous acid, and in the decomposition of the thiocarbazates by alkalis.

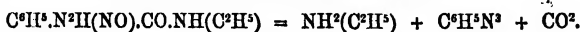
Phenyl-ethyl-semicarbazide, $\text{N}^2\text{H}^2(\text{C}^6\text{H}^5).\text{CO.NH}(\text{C}^2\text{H}^5)$, is formed by direct union of phenyl-hydrazine and ethyl-carbimide:



It dissolves in hot alcohol, and separates therefrom in well-formed monoclinic tabular crystals, exhibiting the combination $\infty \text{P} . 0\text{P} . + \text{P} . \infty \text{R}$ (fig. 7). Axes $a : b : c = 0.8268 : 1 : 1.1457$. Angle $ac = 61^\circ 0'$. Plane of the optic axes parallel to the plane of symmetry. First median line in the acute angle ac . It melts at 151° . Heated to 100° with strong hydrochloric acid, it is resolved into ethylamine, phenyl-hydrazine and carbon dioxide:

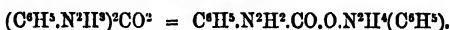


Nitrous acid converts it into a nitroso-derivative, $\text{C}^6\text{H}^5.\text{N}^2\text{H}(\text{NO}).\text{CO.NH}(\text{C}^2\text{H}^5)$, which crystallises in slender yellow needles, melts at 86.5° , and is decomposed by boiling with alkalis into ethylamine, diazobenzenimide and carbon dioxide, according to the equation:



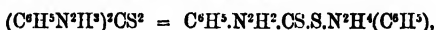
Phenyl-semicarbazide, $\text{N}^2\text{H}^2(\text{C}^6\text{H}^5).\text{CO.NH}^2$, obtained by the action of potassium cyanate on a normal salt of phenyl-hydrazine, crystallises in colourless plates melting at 170° . It is analogous to the preceding compound in all its reactions.

Phenyl-hydrazine Phenyl-carbazate,



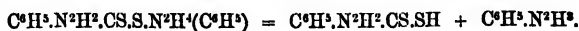
Phenyl-hydrazine absorbs dry carbon dioxide very readily, and solidifies to a white crystalline mass having this composition. The same compound is more easily prepared by saturating a cooled emulsion of 1 pt. phenyl-hydrazine and 10 pts. water with carbon dioxide, and may be obtained by rapid filtration, pressure between filter-paper, and washing with ether, as a white crystalline mass, soft to the touch, and having a rather strong odour recalling that of phenyl-hydrazine. It dissolves sparingly in water and in ether, easily in alcohol, from which, however, it cannot again be separated. Acids and hot water decompose it readily. On exposure to the air, it gives off carbon dioxide, and deliquesces to an oily red-brown mass. It volatilises easily in a stream of carbon dioxide, and immediately reduces Fehling's solution.

Phenyl-hydrazine Phenyl-thiocarbazate,



is formed in like manner by direct addition of CS^2 to phenyl-hydrazine, the combination taking place at ordinary temperatures and being attended with considerable evolution of heat, on which account it is necessary to mix the base with 4 vol. ether before adding the carbon disulphide, otherwise decomposition will ensue. The liquid boils up violently, and the salt immediately separates in the solid form; it may be obtained pure by filtering and washing with ether. It is sparingly soluble in ether, carbon sulphide, chloroform, and ligroin, easily in warm acetone, and crystallises from ether by spontaneous evaporation in six-sided tablets or prisms. The freshly prepared substance, when quickly heated in a capillary tube, melts between 96° and 97° , with slight evolution of gas, to a slightly yellow liquid; by slower heating, on the other hand, it is completely decomposed, without fusion, at a much lower temperature.

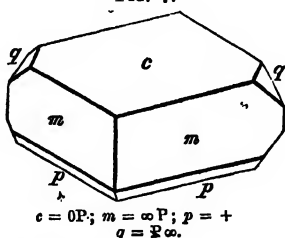
The position of the sulphur-group in the constitutional formula above assigned to this salt is analogous to that which it occupies in the thiocarbamates, and is further justified by the resolution of the compound, under the influence of acids, into phenyl-hydrazine and phenyl-thiocarbazic acid:



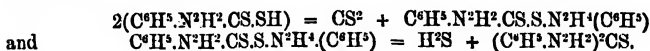
Phenyl-thiocarbazic acid, $\text{C}^6\text{H}^5.\text{N}^2\text{H}^2\text{S}^2$, is precipitated, on adding dilute sulphuric acid to a solution of the phenyl-hydrazine salt in dilute aqueous potash, in thin shining laminae, which have at first a greenish colour, arising from admixture with a dark colouring matter, but may be purified and rendered quite white by filtration, pressure, stirring up with the smallest possible quantity of absolute alcohol, and repeated filtration.

This compound possesses marked acid properties, dissolving easily and without

FIG. 7.



decomposition in alkalis, but no definite salts have yet been obtained from it. It dissolves readily in ether, acetone, glacial acetic acid and alcohol, but decomposes in these solutions with extraordinary facility into the phenyl-hydrazine salt and free carbon disulphide. The same decomposition takes place, though much more slowly, in the dry state at ordinary temperatures, quickly at a moderate heat, but the phenyl-hydrazine salt is then further resolved into H^2S and diphenyl-thiocarbazide:



Diphenyl-thiocarbazide, $(\text{C}^6\text{H}^5.\text{N}^2\text{H}^2)\text{CS}$. To prepare this compound, the crude salt obtained by combination of phenyl-hydrazine and carbon disulphide (p. 1055) is freed from ether by pressure and drying in contact with the air, then finely pulverised and heated to 110° - 140° in an oil-bath, in layers of moderate thickness, whereupon it fuses, swells up, and gives off large quantities of hydrogen sulphide. The gaseous products of the decomposition are removed by a stream of carbon dioxide, the action of the heat being assisted by occasional stirring of the pasty mass, and the operation is interrupted as soon as the odour of hydrogen sulphide is replaced by that of ammonia. The greenish melt thus obtained solidifies on cooling to a crystalline mass; and on pulverising this mass, exhausting it with absolute alcohol, which dissolves the greater part of the secondary products, and recrystallising the residue from hot alcohol—prolonged boiling being avoided as much as possible—the thiocarbazide is obtained in hard colourless triangular prisms.

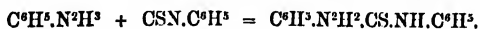
Diphenyl-thiocarbazide dissolves sparingly in alcohol, acetone, chloroform, benzene, and glacial acetic acid, sparingly at ordinary, more readily at higher temperatures; aniline also dissolves it with the aid of heat, forming a solution of deep green colour in thin layers, dark red in thicker layers. The solution in glacial acetic acid also becomes green to dark red on boiling, and the same coloration is produced, though slowly, in the solutions of the thiocarbazide in hot alcohol, benzene, and chloroform—further, though in a lesser degree, by the action of heat on the dry substance. The red colouring matter is, however, most easily produced by the agency of dilute aqueous or alcoholic potash, which dissolves the thiocarbazide readily at a gentle heat, forming a dark red solution which, on acidulation, deposits the colouring matter in blue-black flocks. On separating these by filtration, dissolving them in warm chloroform, and precipitating with alcohol, the colouring matter is obtained in blue-black slender microscopic needles.

The analysis of this red colouring matter leads to the formula $\text{C}^{13}\text{H}^{12}\text{N}^4\text{S}$, according to which it contains 2 atoms of hydrogen less than diphenyl-thiocarbazide; but as the analytical differences between the two bodies are but small, and the mode of formation of the red substance, in which the conditions of oxidation can scarcely be said to be present, gives no account of the removal of these two hydrogen-atoms, it is more probable that the red substance is an isomeride of diphenyl-thiocarbazide, produced therefrom by atomic transposition. It is to some extent analogous to Baeyer's phenol-colouring matters, and to the nitrogenous colouring matters which Liebermann obtained by the action of nitrous acid on phenol and its homologues (*2nd Suppl.* 901).

The solution of the red colouring matter in chloroform is splendidly dichroic, the dark red of the thicker strata passing, on dilution, into a bright green of great intensity. The same solution when treated with bromine, yields substitution-products, characterised by the brilliant metallic reflection of the solid substance.

The alkaline solution of the red substance is quickly reduced by zinc-dust; yielding a colourless liquid, which becomes violet-red on exposure to the air; and on acidifying this red solution, a new colouring matter is precipitated in the form of red crystalline flocks.

Diphenyl-thiosemicarbazide, $\text{C}^6\text{H}^5.\text{N}^2\text{H}^2.\text{CS.NH.C}^6\text{H}^5$, is prepared by mixing the alcoholic solutions of phenyl-hydrazine and phenyl-thiocarbimide:



It immediately separates in the crystalline form, and may be obtained by one crystallisation from alcohol in colourless prisms. It is insoluble in water, slightly soluble in ether, carbon disulphide and ligroin, more readily in acetone, hot alcohol, and glacial acetic acid, and separates from most of these solvents in stellate groups of slender prisms. It melts at 177° , and, like most salts and derivatives of phenyl-hydrazine, becomes strongly electric by friction. It dissolves in dilute aqueous alkalis easily but without coloration, and is precipitated from the solution by acids in its original state. The stability of this body in alkaline solution shows that it differs in constitution from diphenyl-thiocarbazide and that both the hydrazine-

groups of the latter concur in the formation of the colouring matter produced from it by the action of alkalis. By prolonged boiling with strong hydrochloric acid, diphenyl-thiosemicarbazide is resolved, like thiocarbamilide, into its generators, phenyl-hydrazine and thiocarbimide. Its hot alcoholic solution immediately reduces mercuric oxide, acquiring a dark red colour, and depositing on cooling, crystalline flocks of the same colour, the composition of which has not been ascertained.

Paratolyl-hydrazine, $C^7H^{10}N^2 = C^7H^7.N^2H^3 = C^7H^4(CH^3).NH.NH^2$, $[CH^3 : N^2H^3 = 1 : 4]$, is prepared from paratoluidine in the same manner as phenyl-hydrazine from aniline (p. 1048), and crystallises from the ethereal solution of the crude product, on cooling to a low temperature, in thin white laminae. It melts at 61° , and boils, with slight decomposition, at 240° – 244° ; dissolves readily in alcohol, ether, and benzeno, sparingly in water. *Dibenzoyl-tolyl-hydrazine* melts at 188° (Fischer, *Ber.* viii. 589; ix. 890).

B. SECONDARY AROMATIC HYDRAZINES.

The primary hydrazines being formed by substitution of an alcohol-radicle for one atom of hydrogen in the group NH^2-NH^2 , it is easy to see that the introduction of a second alcohol-radicle may give rise to two isomeric secondary derivatives, accordingly as the two alcohol-radicles are attached to the same or to different atoms of nitrogen. To the latter class belong the well-known hydrazo-compounds, $R-NH-NH-R'$, e.g. hydrazobenzene (1st Suppl. 209, 271); to the former the unsymmetrical bases $R \begin{smallmatrix} R \\ \text{R} \end{smallmatrix} > N-NH^2$, which we have now to consider.

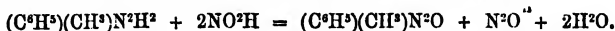
The two isomeric derivatives of each pair are in all probability formed simultaneously by the action of alcoholic bromides on the primary hydrazines, but it has not yet been found possible to separate them. The unsymmetrical secondary bases are much more readily obtained, and indeed as sole products, by reduction of the nitrosamines of secondary amines, e.g. ethyl-phenyl-nitrosamine or nitrosoethyl-aniline, $C^6H^5N(C^2H^5)NO$, prepared by the action of nitrous acid on ethyl-aniline dissolved in dilute hydrochloric acid, or of potassium nitrito on ethyl-aniline hydrochloride (p. 206).

Methyl-phenyl-hydrazine, $(C^6H^5)(C^2H^5)N-NH^2$. To prepare this base, 30 grams of methyl-phenyl-nitrosamine dissolved in 120 grams of 50 per cent. acetic acid and the requisite quantity of alcohol, are added gradually and with agitation to 200 grams of cooled 90 per cent. alcohol in which 150 grams of zinc-dust are suspended, the temperature not being allowed to rise above 30° . The products of several such operations are united, filtered, and supersaturated with strong soda-ley; and the resulting solution is either distilled with steam, or directly exhausted with ether. The ether-alcoholic extract is acidulated with sulphuric acid and evaporated—the acidulation being necessary to prevent the volatilisation of the base with the alcohol-vapour;—the aqueous residue is supersaturated with soda-ley; the oil which then separates is dried with potassium carbonate and distilled; and the fraction which passes over between 190° and 240° is left to stand in shallow vessels over sulphuric acid to free it from ammonia. The residue thus obtained is a mixture of methyl-phenyl-hydrazine, and methyl-aniline, which may be separated by converting them into sulphates and crystallising these salts from alcohol, in which the hydrazine salt dissolves less easily than that of methyl-aniline. For this purpose the crude base is mixed with the calculated quantity of sulphuric acid; the mixture is cooled to 0° and diluted with an equal volume of absolute alcohol; the crystalline mass which separates is filtered on a vacuum-filter, and the residue, after washing with alcohol, is freed as far as possible from mother-liquor by pressure between filter-paper, whereupon the greater part of the methyl-aniline salt passes into solution, still however mixed with a not inconsiderable quantity of methyl-phenyl-hydrazine. The mixture of bases obtained by supersaturating the mother-liquor with soda-ley, may be utilised for the preparation of substitution-derivatives of methyl-phenyl-hydrazine, which are more easily separated from the methyl-aniline. The separated sulphate of methyl-phenyl-hydrazine may be completely purified by once recrystallising it from absolute alcohol, and drying the white crystalline mass at 100° . The aqueous solution of this purified salt supersaturated with a strong alkali, yields the base in the form of an oil, which may be dried with potassium carbonate and rectified.

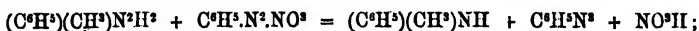
Methyl-phenyl-hydrazine is an oily liquid, colourless when freshly prepared, but soon becoming dark-brown by oxidation when exposed to the air. It remains liquid at -17° and boils at 222° – 224° (bar. 715 mm.) which is 10° lower than the boiling

point of phenyl-hydrazine. In this respect it differs from the ordinary amine-bases—in which the introduction of each successive alcohol-radicle is attended with a rise in the boiling point—but resembles the substituted carbamides. It dissolves sparingly in cold, more readily in hot water, and mixes in all proportions with alcohol, ether, chloroform, benzene, and carbon disulphide. Towards oxidising agents it exhibits greater stability than phenyl-hydrazine. Its *sulphate*, $(C^6H^5N^2H(CH^3)SO_4)$, forms thin white shining laminae. The other salts are very soluble in water, and in alcohol, and difficult to obtain in the crystallised state. Methyl-phenyl-hydrazine, like phenyl-hydrazine, unites with 1 mol. bromide or iodide of ethyl to form well-crystallised azonium-compounds.

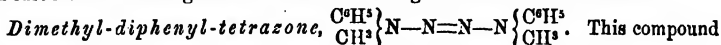
By the action of nitrous acid on the salts of methyl-phenyl-hydrazine, the base is resolved into methyl-phenyl-nitrosamine and nitrogen monoxide:



Methyl-phenyl-hydrazine in excess, and diazobenzene nitrate mixed up to an emulsion with water, act on one another rapidly at ordinary temperatures, producing methyl-aniline, diazobenzenimide and nitric acid:



and further the oxidising action of the nitric acid gives rise to the formation of



is likewise obtained, and more readily, by gradually adding small quantities of mercuric oxide to a solution of methyl-phenyl-hydrazine (best of the crude product) in eight times its quantity of chloroform. The solution, which must be well cooled, becomes dark brown, and the reaction is complete when the liquid, after being left at rest, no longer gives off gas. The filtered solution is evaporated to a small bulk, mixed with alcohol, and the crystalline mass which separates is pressed and re-crystallised from alcohol, to which a little zinc-dust and a very small quantity of glacial acetic acid have been added to promote decolorisation. By repeated crystallisation from alcohol, the tetrazone is obtained in thin colourless laminae which melt with decomposition at 133° . It dissolves easily in carbon sulphide, sparingly in cold alcohol and ether; is not altered by hot water, or by oxidising or reducing agents. Acids added to its alcoholic solution resolve the compound into nitrogen and methyl-aniline, the liquid becoming deep blue. In chloroform solution it unites with *iodine*, forming the compound $C^6H^5N^4 + 4I$, which consists of black microscopic needles, is very slightly soluble in chloroform, and very unstable, detonating when dry even at the ordinary temperature of a room; and decomposed by molecular silver into silver iodide and the tetrazone. The iodine-compound is also readily decomposed by dilute alkalis.

Derivatives of Methyl-phenyl-hydrazine.

This base acts with *benzoyl chloride* and *benzaldehyde* in the same way as phenyl-hydrazine (p. 1052), forming crystallisable compounds; it is strongly attacked by acetic anhydride and ethyl isocyanate. It does not unite with *carbon disulphide* at ordinary temperatures; but on applying heat, hydrogen sulphide is evolved and the mixture solidifies to a crystalline mass.

Methyl-phenyl-semicarbazide, $\left. \begin{matrix} C^6H^5 \\ CH^3 \end{matrix} \right\} N-NH-CO-NH^2$, is formed on mixing a concentrated solution of the crude base containing a slight excess of hydrochloric acid with an equivalent quantity of pure potassium cyanate, and separates as a dark brown oil which gradually crystallises on cooling. It may be purified by pressure between bibulous paper and solution in the smallest possible quantity of hot benzene, from which it partly crystallises on cooling, and the rest may be precipitated by ether. By repeating these operations, the compound is obtained as a dazzling white mass of slender crystals. It melts at 133° , dissolves readily in hot water, alcohol, and hot benzene, less readily in ether, ligroin, and cold water. With strong hydrochloric acid, it forms an unstable hydrochloride; heated to 100° with hydrochloric acid, it is resolved into ammonia, carbon dioxide, and methyl-phenyl-hydrazine. Fehling's solution does not act upon it; silver nitrate only at the boiling heat. With *nitrous acid* it yields a nitroso-derivative, $(C^6H^5)(CH^3)N.N(NO)CO.NH^2$, which crystallises in thin laminae having a golden lustre; melts at 77° ; is slightly soluble in water, and forms Liebermann's colouring matters with phenol and sulphuric acid (2nd Suppl. 901).

Methyl-diphenyl-thiosemicarbazide, $(C^6H^5)(CH^3)N.NH.CS.NH(C^6H^5)$, prepared from methyl-phenyl-hydrazine and phenyl-thiocarbimide, melts at 154° and dissolves readily in hot alcohol, chloroform, and benzene. The boiling chloroform solution is desulphurised by yellow mercuric oxide.

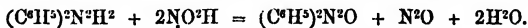
Diphenyl-hydrazine, $C^{12}H^{12}N^2 = (C^6H^5)^2N-NH^2$. This base, metameric with hydrazobenzene (1st Suppl. 209, 271), is formed by the action of zinc and glacial acetic acid on an alcoholic solution of diphenylnitrosamine (p. 209), the acetic acid being added by small portions and the vessel kept cool. When the action is complete, the liquid is filtered, concentrated to one-fourth of its bulk, then diluted with an equal volume of water, and mixed gradually with a large excess of fuming hydrochloric acid, the mixture being all the while kept cool and stirred. On cooling, the hydrochloride, which is but very slightly soluble in strong hydrochloric acid, separates out in blue needles contaminated with diphenylamine, which is produced simultaneously with the hydrazine base, but may be easily removed by recrystallising the crude product from hot very dilute hydrochloric acid, the greater part of the diphenylamine remaining as an oil. The hydrazine base may then be reprecipitated from the filtrate by strong hydrochloric acid, and by repeating these operations several times, the hydrochloride is obtained quite free from diphenylamine. It is still, however, slightly blue, but by recrystallisation from hot alcohol it may be obtained in slender colourless needles.

Diphenyl-hydrazine, separated from the pure hydrochloride by caustic soda, is a faintly yellow oil which becomes viscid at -7° , but does not solidify. When heated it partly volatilises undecomposed, and is partly resolved into ammonia, diphenylamine, and non-volatile resinous products. It dissolves very easily in ether, alcohol, benzene, and chloroform, very sparingly in water. It is a mono-acid base, but its salts are much less stable than those of phenyl-hydrazine and methylphenyl-hydrazine, being partially decomposed even by water. The hydrochloride forms white needles very slightly soluble in cold water and in strong hydrochloric acid. The aqueous solution, saturated in the cold, becomes turbid on warming, from separation of the base, but clear again as it cools; the solution in dilute hydrochloric acid is quite stable. The sulphate, $[(C^6H^5)^2N^2H^2]^2SO^4$, is moderately soluble in hot dilute sulphuric acid, and separates on cooling in needles mostly having a blue tint; like the hydrochloride, it is partially decomposed by pure water. The nitrate crystallises in slender needles sparingly soluble in cold, somewhat more freely in hot water.

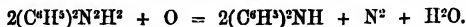
Diphenyl-hydrazine is distinguished from the isomeric body hydrazobenzene, $C^6H^5.NH-NH.C^6H^5$, by its behaviour to nitrous acid and to oxidising agents, and by its capability of forming substitution-products by the entry of alcohol- or acid-radicles into the nitrogen group N^2H^2 ,—a substitution which, though theoretically possible in the case of hydrazobenzene, has not been actually effected.

Action of Nitrous Acid.—Hydrazobenzene, as shown by Baeyer (*Ber.* ii. 683), when treated with nitrous acid, in an alcoholic solution cooled by ice, is converted into a nitroso-compound, probably $C^6H^5-N(NO)-(NO)N-C^6H^5$, which is decomposed, partially at ordinary temperatures, and completely with slight detonation when gently heated, into nitrogen dioxide and azobenzene.

Diphenyl-hydrazine, on the other hand, is decomposed by nitrous acid, similarly to methylphenyl-hydrazine, into diphenylnitrosamine and nitrogen monoxide:



Oxidation.—Hydrazobenzene, under the influence of oxidising agents, is easily and completely converted into azobenzene. The mode of oxidation of diphenyl-hydrazine varies—as in the case of the hydrazines previously described—according to the reagents used, the temperature, and the concentration of the solutions. By *Fehling's solution*, the base, on account of its sparing solubility in water, is but very slowly attacked, even with the aid of heat. By *mercuric oxide*, *silver oxide*, and *ferric chloride*, oxidation is rapidly effected even in the cold, and at higher temperatures the greater part of the base is resolved into nitrogen and diphenylamine, perhaps according to the equation



At the same time there is formed a greater or smaller quantity of a blue-violet nitrogenous colouring matter easily soluble in alcohol, the composition of which has not yet been determined. If, on the other hand, the oxidation takes place in the cold, and in very dilute solution, there is formed, together with products just mentioned, a variable quantity of a compound, $C^{12}H^{12}N^4$, which, from its resemblance to dimethyl-phenyl-tetrazone (p. 1058), may be called tetraphenyl-tetrazone, and represented by the constitutional formula, $(C^6H^5)^2N-N=N-N(C^6H^5)^2$.

This compound is most readily prepared by agitating diphenyl-hydrazine with a very dilute solution of ferric chloride, as neutral as possible and well cooled, whereupon the liquid assumes a blue-violet colour, and gradually solidifies to a crystalline mass, the reaction being complete when the product has become perfectly solid. This crude product is washed on a filter, first with water, then repeatedly with alcohol, which removes diphenylamine and colouring matter, leaving the tetrazone as a slightly coloured crystalline mass, which may be further purified by rubbing it to powder, boiling it with small quantities of alcohol, and recrystallising it several times from pure warm carbon disulphide.

Tetraphenyl-tetrazone melts at 123° to a yellow liquid, with evolution of gas, and formation of diphenylamine and non-volatile products. It dissolves sparingly in ether, alcohol, chloroform, and ligroin, with moderate facility in warm carbon disulphide. When drenched with concentrated acids, it turns blue and slowly dissolves, decomposing at the same time; on heating the liquid the blue colour changes to dingy green.

Benzoyldiphenyl-hydrazine, $C^{10}H^{16}N^2O = (C^6H^5)^2N^2.H.CO.C^6H^5$. This compound is obtained by gradually adding 1 mol. benzoyl chloride to a solution of 2 mol. diphenyl-hydrazine in a ten-fold quantity of ether, washing the crystalline mass which separates with slightly acidulated water to remove diphenyl-hydrazine hydrochloride, and crystallising the residue from hot acetone. The benzoyl-derivative then separates in white slender needles having a vitreous lustre. It dissolves easily in hot acetone and chloroform, less easily in alcohol and ether. It melts at 192° , and decomposes at a higher temperature. By concentrated acids it is slowly resolved into benzoic acid and diphenyl-hydrazine.

Benzylidene-diphenyl-hydrazine, $C^{10}H^{16}N^2 = (C^6H^5)^2N^2.CH.C^6H^5$, is formed on mixing diphenyl-hydrazine and benzaldehyde in molecular proportions. This solution immediately becomes turbid, from separation of water, and on cooling solidifies to a crystalline mass of the benzylidene-compound, which may be purified by recrystallisation from hot alcohol.

Benzylidene-diphenyl-hydrazine forms small crystals mostly having a faint yellow colour, and no very characteristic form. It is easily soluble in ether, chloroform, and benzene, slightly soluble in cold water. Its melting point is 122° , which is remarkable as being lower by 30° than that of benzylidene-monophenyl-hydrazine (p. 1053).

Ethyl-derivatives of Phenyl-hydrazine. It has already been observed (p. 1051) that, by the action of ethyl-bromide on phenyl-hydrazine, there is formed, in addition to phenyl-diethylazonium bromide, $C^6H^5.N^2H^2(C^2H^5)(C^2H^5Br)$, a mixture of volatile bases. These cannot be separated from one another by fractional distillation, but their separation may be effected by taking advantage of the different behaviour of the several substituted hydrazines towards oxidising agents, especially mercuric oxide, the primary bases being thereby completely decomposed, with evolution of nitrogen, the unsymmetrical secondary bases converted into indifferent tetrazone-compounds (pp. 1058, 1059), and the symmetrical secondary bases (hydrazo-compounds) into azo-compounds, while the tertiary bases remain unaltered.

The crystallised mixture of hydrobromides obtained by warming phenyl-hydrazine and ethyl bromide in molecular proportions, is dissolved in water and mixed with alkali; the oily bases thereby separated are dissolved out with ether; and the residue left on evaporating the ether is mixed with strong hydrochloric acid to remove unaltered phenyl-hydrazine. The filtrate contains the whole of the volatile ethyl-bases, which, after addition of alkali, may again be extracted with ether, and at once treated in this solution with an excess of yellow mercuric oxide. The dark brown solution resulting from the oxidation is shaken up with dilute hydrochloric acid to remove basic products consisting of a tertiary hydrazine base not yet examined, together with small quantities of aniline and ethylaniline; and on evaporating off the ether from the remaining liquid, there remains a dark-coloured oily residue which, after a while, solidifies partially to a crystalline mass; and this, when separated from the mother-liquor, and repeatedly crystallised from hot alcohol, is obtained quite white, and has the composition of diethyl-diphenyl-tetrazone, $(C^6H^5)^2(C^2H^5)^2N^4$.

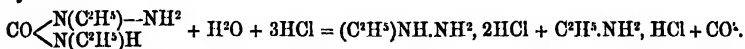
The non-crystallising oily product distilled with steam yields a light yellow oil smelling strongly like phenyl cyanide, and consisting chiefly of azophenylethyl, $C^6H^5.N=N.C^2H^5$, the nitro-derivative of which was obtained by Meyer & Ambühl by the action of diazobenzene sulphate on sodium nitroethane (p. 137).

Azophenyl-ethyl volatilises without decomposition, is not acted on by dilute acids, is dissolved without alteration by strong hydrochloric acid at ordinary temperatures, but completely decomposed when heated therewith. It unites with iodine dissolved in carbon sulphide, forming a dark-coloured, heavy uncrystallisable oil. It is not altered by Fehling's solution, even at the boiling heat, but when treated in alcoholic solution with zinc-dust and acetic acid, or zinc and hydrochloric acid, it is completely converted

into ethyl-phenyl-hydrazine, $C^6H^5.NH.NH.C^2H^5$. This base distils without decomposition; reduces Fehling's solution at a gentle heat; forms easily soluble salts; and is reconverted by mercuric oxide into the azo-compound (W. Ehrhardt a. E. Fischer, *Deut. Chem. Ges. Ber.* xi. 613).

C. HYDRAZINES OF THE FATTY SERIES.

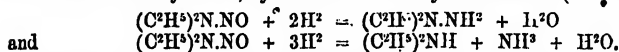
Ethyl-hydrazine, $C^2H^5.NH.NH^2$ (E. Fischer, *Deut. Chem. Ges. Ber.* ix. 111). This compound is obtained from diethyl-nitrosocarbamide, $(C^2H^5)NH.CO.N(C^2H^5).NO$ (see CARBAMIDES, p. 390), by reducing that compound in alcoholic solution with zinc-dust and acetic acid to diethyl-hydrazine-carbamide, $(C^2H^5)NH.CO.N(C^2H^5).NH^2$, and heating the latter with strong hydrochloric acid, whereby it is resolved into carbon dioxide, ethylamine, and ethyl-hydrazine:



The dihydrochloride of ethyl-hydrazine crystallises in needles which give off part of their hydrochloric acid when warmed, leaving a syrupy salt, probably the monohydrochloride, closely resembling that of diethyl-hydrazine. The free base volatilises without decomposition, dissolves easily in water and in alcohol, smells strongly ammoniacal, and exhibits reactions exactly analogous to those of phenyl-hydrazine.

The hydrazines of the fatty group containing two alcohol-radicles are produced by reduction of the corresponding nitrosamines with zinc-dust and acetic acid (E. Fischer, *Deut. Chem. Ges. Ber.* viii. 1587; xi. 2206).

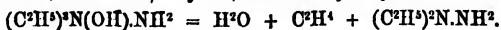
Diethyl-hydrazine, $C^2H^5)^2N.N^2 = (C^2H^5)^2N.NH^2$, is formed, together with ammonia and diethylamine, by reduction of diethyl-nitrosamine (2nd Suppl. 861).



The action begins at ordinary temperatures, and may easily be regulated by gradual addition of the zinc and acetic acid; towards the end however it must be assisted by gently heating the liquid till the pungent odour of the nitrosamine is no longer perceptible. The liquid is then filtered, supersaturated with potash, and distilled; the distillate containing the three bases is neutralised with hydrochloric acid and evaporated to a syrup, whereby the ammonia is almost completely removed in the form of a crystalline mass of sal-ammoniac, easily separated from the deliquescent hydrochlorides of the other two bases; and the filtrate treated with solid potassium hydrate and calcined pearl-ash yields a light nearly colourless oil consisting of diethylamine and diethyl-hydrazine.

These two bases are separated by means of ethyl iodide, with which the hydrazine unites directly to form triethylazonium iodide, $(C^2H^5)^3N^+H^2.C^2H^5I^-$, whilst the diethylamine, if the process is carefully conducted, is converted, first into triethylamine, and only at a later stage into tetrethyl-ammonium iodide. The formation of this last compound must however be prevented as far as possible, since its subsequent separation from the tetrethyl-azonium compound does not appear to be possible. The best way of proceeding is to treat 10 grams of the mixed bases with the calculated quantity of ethyl iodide; heat the mixture gently in a reflux apparatus; cool the vessel externally as soon as the liquid becomes strongly heated by the reaction; and then add water. The undecomposed ethyl iodide thereby separated is dissolved out by ether; the remaining aqueous solution, after addition of potash is freed from volatile bases by distillation; and on mixing the residual liquid with strong potash-ley, the triethylazonium iodide is precipitated as a colourless oil which soon solidifies, and may be purified by crystallisation from hot alcohol.

This compound, $(C^2H^5)^3NI.NH^2$, crystallises in slender white needles, easily soluble in water and in hot alcohol, nearly insoluble in concentrated alkalis, and forms a sparingly soluble double salt with *platinic chloride*. By silver oxide and water it is easily converted into the corresponding hydroxide, which is soluble in water, has a strong alkaline reaction, and is decomposed by heat like the corresponding ammonium hydroxides, into water, ethylene, and diethyl-hydrazine:



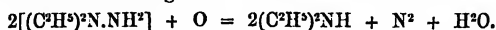
To prepare diethyl-hydrazine in quantity by this process, the aqueous solution of the hydroxide is distilled in an oil-bath, the temperature being ultimately raised to 140° – 150° , whereby a distillate is obtained consisting of an aqueous solution of the

hydrazine, which is to be mixed with hydrochloric acid, concentrated, and decomposed with potash; and the only base thereby separated repeatedly dried over solid potash and distilled.

Diethyl-hydrazine is a colourless mobile liquid having an ammoniacal odour, easily soluble in water, alcohol and ether, sparingly soluble in concentrated alkalis. Its boiling point appears to lie between 74° and 78° ; but this determination must not be regarded as exact, since the base examined contained a small quantity of triethylamine, resulting from the decomposition of the tetrethyl-ammonium iodide formed as above mentioned, simultaneously with the azonium compound.

The salts formed by diethyl-hydrazine with mineral acids are very soluble in water and in alcohol; the *hydrochloride* deliquesces in moist air. The *picrate* is less soluble, and crystallises from a warm solution in slender yellow needles; its aqueous solution decomposes at the boiling heat, with evolution of nitrogen.

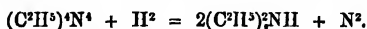
Oxidation.—Diethyl-hydrazine, like the aromatic hydrazines, is decomposed by Fehling's solution, only with the aid of heat, being then resolved for the most part into diethylamine and nitrogen:



By more energetic oxidising agents, on the other hand, mercuric oxide for example, it is converted into tetrethyl-tetrazone, $(C^2H^5)_2N^4 = (C^2H^5)_2N-N \equiv N-N(C^2H^5)_2$, analogous in constitution to the compound $C^2H^5.O-N \equiv N-O.C^2H^5$, which Zorn obtained by the action of ethyl-iodide on nitrosyl-silver (see NITROSO-COMPOUNDS).

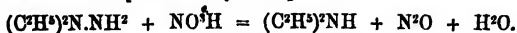
To prepare tetrethyl-tetrazone, a cold aqueous solution of diethyl-hydrazine (the crude product answers best) is gradually mixed with yellow mercuric oxide, till the latter is no longer reduced. The liquid then becomes turbid from separation of an oil, which on agitation is for the most part taken up by the porous mass of mercury-compounds. The aqueous solution is filtered off, and the residue repeatedly washed on the filter with small quantities of alcohol, whereby the tetrazone is dissolved, and separates again in the watery filtrate: it is then separated and dried over calcium chloride.

Tetrethyl-tetrazone thus purified is an oily liquid having a faint yellow colour and peculiar alliaceous odour. It remains liquid at -17° , and is not volatile even in a vacuum. Heated to 135° – 140° in a capillary tube, it decomposes slowly, with evolution of gas; when a larger quantity is quickly and strongly heated, it detonates slightly, and is resolved into nitrogen, diethylamine, and a pungent substance not yet examined. It has decided basic properties; being easily dissolved by dilute acids in the cold, and separated therefrom by alkalis in its original state. Its *platinochloride*, $2(C^2H^5)_2N^4.PtCl^6$, separates from a moderately dilute alcoholic solution in long gold-yellow needles. It dissolves in cold water without alteration, but on boiling the solution, it is decomposed, giving off half its nitrogen as gas, and yielding at the same time diethylamine and aldehyde. The same decomposition takes place when the tetrazone itself is heated with mineral acids, the resulting solution containing diethylamine, together with variable quantities of aldehyde and a pungent substance not yet examined. The formation of diethylamine and nitrogen is represented by the equation:



Tetrethyl-tetrazone precipitates many of the salts of the heavy metals, and unites with *mercuric chloride*, forming a white, crystalline, slightly soluble mass having the composition $(C^2H^5)_2N^4.HgCl^2$. It is easily oxidised by *silver salts*; on shaking up a cold emulsion of the tetrazone with silver nitrate, an evolution of gas takes place almost immediately, accompanied by the formation of a silver speculum. Silver oxide attacks it only when aided by heat. With *iodine* it forms an explosive compound, which separates, on agitating a solution of iodine in potassium iodide with small quantities of the base, as a dark-coloured oil which detonates even at a gentle heat.

Action of Nitrous Acid.—Diethyl-hydrazine is completely decomposed by nitrous acid at ordinary temperatures, the product consisting for the most part of nitrogen monoxide and diethylamine, together with a small quantity of tetrethyl-tetrazone. The principal reaction is represented by the equation:



Diethyl-carbazide, $(C^2H^5)_2N.NH.CO.NH^2$, is formed by the action of potassium cyanate on the neutral salts of diethyl-hydrazine. It is easily soluble in water, but may be extracted by ether from a solution strongly supersaturated with potash, and crystallises in large thin plates. With platinic chloride it forms a double salt $[(C^2H^5)_2N^2H.CO.NH^2]_2PtCl^6$, which crystallises from alcohol in slender yellow needles.

Diethyl-carbazide is resolved by prolonged boiling with alkalis into carbon dioxide, ammonia, and tetrethyl-hydrazine. Nitrous acid converts it into an oily unstable nitroso-derivative.

Dimethyl-hydrazine, $(\text{CH}_3)_2\text{N}.\text{NH}_2$, formed by reducing dimethyl-nitroformamine with zinc-dust and acetic acid, is a light volatile liquid, having an ammoniacal odour, dissolving easily in water, alcohol, and ether, and reacting with Fehling's solution in the same manner as the aromatic hydrazines, but less readily; it is also more stable in presence of alkalis. Its haloïd salts volatilise without decomposition. The *hydrochloride* crystallises from alcohol and is very hygroscopic. Its *platinochloride* has the composition $[(\text{CH}_3)_2\text{N}-\text{NH}_2.\text{HCl}]^2\text{PtCl}_4$ (Fischer, *Ber.* ix. 111).

HYDRAZOBENZENE (DICHLORO-). See BENZENE-DERIVATIVES (p. 216).

HYDRAZOBENZENE-SULPHONIC ACID. See SULPHONIC ACIDS.

HYDRAZOBENZOIC ACID. See BENZOIC ACID (AZOXY-) (p. 275).

HYDRAZOINDOLE. See INDOLE.

HYDRAZOTOLUENE. See TOLUENE.

HYDRIODIC ACID. See IODINE.

HYDROBENZAMIDE, $\text{C}^2\text{H}^{18}\text{N}^2 = (\text{C}^6\text{H}^5.\text{CH})^2\text{N}^2$ (iii. 183). Borodin (*Ber.* vi. 713) regards the transformation of this compound into the isomeric body, amarine, as analogous to the conversion of tertiary amines into secondary and primary amines (2nd Suppl. 57).

Lophine, $\text{C}^{21}\text{H}^{16}\text{N}^2$ (iii. 733) prepared by the dry distillation of hydrobenzamide, is very slowly attacked by alcoholic potash, with formation of ammonia and potassium benzoate. In presence of air, this act of decomposition is accompanied by an evolution of light, which is clearly visible at $+10^\circ$, and increases with the temperature until it attains its maximum intensity at 65° . The luminosity ceases if the air is expelled from the vessel containing the lophine, either by boiling the solution, or by a current of hydrogen. A solution of lophine in glacial acetic acid does not become luminous on oxidation with potassium permanganate.

Hydrobenzamide gives with alcoholic potash a feeble evanescent light. Amarine similarly treated gives a slightly weaker light than lophine, forming at the same time ammonia and a crystalline base which melts at 204° (Radziszewski, *Ber.* x. 70).

HYDROBENZOÏN, $\text{C}^{11}\text{H}^{12}(\text{OH})^2$. See DIPHENYLENE ALCOHOLS (p. 679).

HYDROBILIRUBIN. The substance so named which Maly obtained by reduction of tribromobilirubin (p. 325), is regarded by Hoppe-Seyler as identical with the colouring matter produced by the action of reducing agents on hæmatin (p. 921).

HYDROBILIVERDIN. See BILE-PIGMENTS (p. 325).

HYDROBROMOCUMENYLACRYLIC ACID, $\text{C}^{12}\text{H}^{15}\text{BrO}^2$. See CINNAMIC ACID, HOMOLOGUES OF (p. 502).

HYDROCARBONS. A new and general method of producing hydrocarbons has been discovered by Friedel and Crafts (*Compt. rend.* lxxxiv. 1392, 1450; lxxxv. 74; *J. pr. Chem.* [2], xvi. 233). It consists in treating organic chlorides (bromides or iodides) either alone or mixed with hydrocarbons, with chloride of aluminium, zinc, or iron. When small quantities of anhydrous aluminium chloride are added to *amyl chloride*, hydrochloric acid gas is rapidly evolved, together with hydrocarbons not absorbed by bromine, and the liquid separates into two layers, one of which contains an extremely varied series of hydrocarbons, ranging from highly volatile bodies to products having a boiling point above that of mercury. The lower members belong to the paraffin series $\text{C}^n\text{H}^{2n+2}$, while the higher members are richer in carbon. When the above reaction is made to take place in presence of a hydrocarbon, the product is a combination of the radicle of the organic chloride with the hydrocarbon, less the hydrogen replaced. Thus, on mixing *amyl chloride* with a considerable excess of benzene, adding aluminium chloride by small quantities at a time, and submitting the products to fractional distillation, a liquid is obtained boiling at 185° – 190° , and having the composition and properties of *amyl-benzene*, $\text{C}^6\text{H}^5.\text{C}^5\text{H}^{11}$. By using ethyl iodide instead of *amyl chloride*, *ethyl-benzene* is formed, together with many compounds of high boiling point. Similarly, by operating under suitable conditions with benzene and methyl chloride, toluene and other higher derivatives of benzene are obtained, viz. *xylene*, *mesitylene*, and *durene*. Benzyl chloride and benzene yield diphenylmethane; triphenylmethane is obtained from benzene and chloroform; tetraphenylmethane from benzene and carbon tetrachloride. Similar reactions, though less definite, are obtained with organic bromides and iodides; thus ethyl iodide and benzene yield ethyl-benzene.

Hydrocarbons obtained by the Action of Water and Acids on the Carbides of Iron and Manganese.—Cloez (*Compt. rend.* lxxviii. 1566) has examined the hydrocarbons obtained by the action at a gentle heat of hydrochloric acid diluted with 2 vols. water on spiegeleisen containing 0.04 per cent. combined carbon, 0.06 MnO₂, a small quantity of silicon, and traces of phosphorus and sulphur. The evolved gas was passed through two wash-bottles filled with water, then through an upright vessel containing lumps of pumice soaked in solution of cupric sulphate, and finally through a Woulfe's bottle containing bromine under water. An oil then collected in the wash-bottles, boiling between 118° and 124°, and having the composition of octylene C⁸H¹⁶. The bromine-liquid yielded by distillation, no ethylene bromide, but a liquid having approximately the composition of propylene bromide, C³H⁶Br². The residue of the distillation heated with alcoholic potash, yielded bromheptylene, C⁷H¹⁴Br (b. p. 130°) and bromoctylene, C⁸H¹⁶Br (b. p. 150°). Soft pig iron did not yield any oily hydrocarbon.

Further experiments by Cloez (*ibid.* lxxxvi. 1248) show that neither cold nor boiling water acts on spiegeleisen, but that when superheated steam is passed over the alloy heated to dull redness, hydrogen, carbon dioxide and traces of marsh-gas are produced.

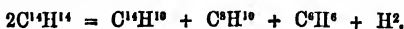
By the action of dilute sulphuric acid on a ferromanganese containing iron 56.5 per cent., manganese 38.2 per cent., and combined carbon 5.0 per cent., large quantities of paraffins and olefines were evolved; pure water, however, acts only at temperatures above 300°. An alloy, which gave by analysis, Mn 85.4, Fe 5.7, Si 1.2, combined carbon 3.7, graphitic carbon 4.0, was readily attacked by water, yielding hydrogen, together with gaseous and liquid hydrocarbons. A similar alloy, containing 81.5 per cent. manganese, when acted on by water at 100°, yielded liquid hydrocarbons and a gas which contained hydrogen mixed with olefines, the products being similar to those formed by the action of dilute acids on cast iron.

From these experiments it follows that when warm water is decomposed by a carbide of manganese and iron, part of the hydrogen set free is evolved as such, while the remainder combines with the carbon to form hydrocarbons, the metals being oxidised to monoxides.

See also F. H. Williams (*Ber.* vi. 834).

Hydrocarbons from Fatty Acids.—Hydrocarbons of the paraffin series are obtained from the products of destructive distillation of the fatty acids, by agitating the crude distillates with strong sulphuric acid, treating the oil which rises to the surface with strong sulphuric acid, then drying and rectifying it. In this way, paraffins are obtained containing from 5 to 11 atoms of carbon (Cahours a. Demarçay, *Compt. rend.* lxxx. 1568).

Decomposition of Hydrocarbons by Heat. Barbier has studied the action of heat on hydrocarbons by heating them to low redness (not above 500°) in exhausted combustion-tubes protected by iron-plate. The decomposition thus effected he finds to be more definite than that which takes place when the hydrocarbons are passed through red-hot tubes. *Dibenzyl* thus treated is completely resolved into stilbene and toluene: $2C^{14}H^{14} = C^{14}H^{12} + 2C^7H^8$. *Stilbene* yields phenanthrene and toluene: $3C^{14}H^{12} = 2C^{14}H^{10} + 2C^7H^8$. The decomposition of *tolane* is less definite, yielding a large quantity of bulky charcoal, impregnated with a hydrocarbon which melts below 100° and smells strongly of diphenyl, together with a small quantity of benzene. *Solid ditolyl*, C¹⁴H¹⁴ (from bromotoluene and sodium), heated to 500° remains unaltered for many hours, but is ultimately decomposed, with deposition of charcoal; no anthracene or phenanthrene is produced. *Liquid ditolyl* (b. p. 280°–285°) heated to redness for five minutes is completely resolved into anthracene, toluene and hydrogen, $2C^{14}H^{14} = C^{14}H^{10} + 2C^7H^8$; a small quantity of phenanthrene is produced at the same time, probably from an isomeric ditolyl. A mixture of *ethylene* and *diphenyl-vapour* passed through a red-hot porcelain tube yields, together with benzene, cinnamene and naphthalene, a mixture of phenanthrene and anthracene, in which the former predominates. The reaction therefore takes place partly according to the equation, $C^{12}H^{10} + C^8H^8 = C^{14}H^{10} + 2H^2$. *Benzyl-toluene* is resolved by heat into anthracene and toluene: $2C^{14}H^{14} = C^{14}H^{10} + 2C^7H^8 + H^2$. A small quantity of phenanthrene appears also to be formed. In products which Berthelot obtained in his investigation on the action of ethylene and of cinnamene on benzene (*1st Suppl.* 261), Barbier has found both anthracene and phenanthrene. *Phenylstyrene* heated to redness for three minutes yields anthracene, styrene (convertible by chromic acid into terephthalic acid) benzene and hydrogen:



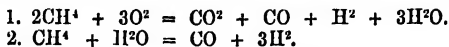
Diphenylmethane heated for five minutes yields anthracene, benzene, and a small

quantity of toluene, but no fluorene: $2C^{10}H^{12} = C^{14}H^{10} + 2C^6H^6 + H^2$, and $C^{10}H^{12} + H^2 = C^6H^6 + C^4H^8$. A small quantity of phenanthrene appears also to be formed. *Phenyl-toluene* (obtained by the action of sodium on a mixture of bromobenzene and liquid bromotoluene) yields when heated, benzene and toluene, but no solid hydrocarbons.

Action of Aqueous Vapour on Hydrocarbons at a Red Heat. (Coquillion, *Compt. rend.* lxxvi. 1197-1200). Dry methane and ethylene are decomposed into carbon and hydrogen by passing over a red-hot spiral of palladium wire, twice the volume of the original gas being formed. In presence of moisture, the carbon of the hydrocarbon unites with the oxygen of the aqueous vapour, forming carbon monoxide, and hydrogen is liberated; the gaseous products in this case occupy four times the volume of the original gas, e.g. $CH^4 + H^2O = CO + 3H^2$.

When a hydrocarbon mixed with a limited supply of oxygen is passed over red-hot palladium, hydrogen, carbon monoxide and dioxide, and water are formed. The amount of carbon monoxide increases and the dioxide diminishes as the supply of oxygen is decreased.

By increasing the quantity of hydrocarbon the reaction may be made to take place in two stages—

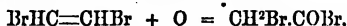


These results explain the action of aqueous vapour on hydrocarbons in the blast furnace.

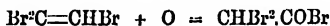
Oxidation. When hydrocarbons mixed with air are passed over red-hot platinum wire, they are oxidised to aldehydes and acids. A mixture of methane and air passed over a platinum spiral ignited by the voltaic current, yielded formic acid, but not formic aldehyde. *Ethylene* was oxidised to acetic acid; *toluene* to benzaldehyde. Palladium acts in this manner still more energetically than platinum, becoming wrinkled and brittle and diminishing in weight (Coquillion, *Compt. rend.* lxxvii. 444).

An aqueous solution of *isopentane* (amyl hydride) containing 1 c.c. of the hydrocarbon to 2 litres of water, mixed with half its volume of a chromic acid mixture composed of 500 pts. water, 5 pts. crystallised chromic anhydride, and 1 pt. potassium dichromate, and left to itself for six weeks at a temperature of 15° to 20° , was found to be completely converted into valeric acid. *Amylene*, on the other hand, treated in like manner, yielded, in addition to carbon dioxide, a mixture of valeric, butyric, propionic, acetic and formic acids (Berthelot, *Compt. rend.* lxxix. 1093). This result differs from those obtained by Chapman & Thorp (*1st Suppl.* 118), who, by oxidising amylene at 80° – 90° with a mixture of 4–8 pts. potassium dichromate, 100 pts. water, and the requisite quantity of sulphuric acid, obtained only acetic and a small quantity of formic acid; and by Truchot (*loc. cit.*) who obtained formic, acetic, propionic, and probably also butyric, but no valeric acid. Berthelot considers that the results obtained by these chemists are not to be explained by the formation of valeric acid in the first instance, and its subsequent oxidation to acids lower in the series, but rather on the supposition that the molecule of amylene presents several points of attack to the oxidising agent, so that sometimes a greater and sometimes a smaller number of oxidation-products may be formed simultaneously.

Oxidation of the Haloid Derivatives of Olefines.—Dibromethylene is converted by agitation with dry oxygen into bromacetyl bromide:



the reaction being attended with a rise of temperature from 15° to 55° . Tribromethylene under the same circumstances also unites with 1 atom of oxygen, forming dibromacetyl bromide:



(Demole, *Ber.* xi. 315).

The compound $CH^2=CHBr$, $CCl^2=CCl^2$ and $CBr^2=CBr^2$, treated with free oxygen in presence of platinum black, are not oxidised at all. Dichloroethylene, $C^2H^2Cl^2$, which Regnault has shown to undergo polymerisation when exposed to the air (*Ann. Chim. Phys.* [2], lxxix. 157), is found to undergo a similar change, with evolution of acid vapours, when shaken up with free oxygen.

The compound $CHCl=CHBr$, which Müller obtained (*Liebig's Annalen*, Suppl. iii. 287) by the action of potassium cyanide on $C^2H^2ClBr^2$, solidifies easily, forming a polymeric modification. This compound, when shaken up with oxygen, yields a large quantity of a fuming liquid boiling at 128° – 132° , and a small quantity of an oily liquid boiling at 140° , besides some unaltered $CHCl=CHBr$. The liquid boiling at 128° – 132° is a mixture of bromacetyl chloride and chloracetyl bromide, as shown

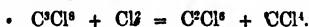
by its boiling point, and by its yielding with water, brom- and chloracetic acids, and with alcohol, ethyl brom- and chloracetates, together with hydrochloric and hydrobromic acids. The oily liquid boiling at 140° is a polymeric modification of $\text{C}^2\text{H}^3\text{ClBr}$, which solidifies on exposure to the air, and carbonises when heated above 100° . Bromamylene, which contains the group CHBr , remains unaltered when treated with free oxygen. From these results the following conclusions may be drawn: 1. If a bromo-, chloro-, or chlorobromo-derivative of ethylene undergoes polymerisation on exposure to the air, it is also capable of absorbing oxygen; and forming an acid compound. 2. If polymerisation does not take place, oxidation cannot. 3. The final products, C^2Cl^4 and C^2Br^4 , since they contain no hydrogen, can neither be oxidised, nor can they form polymerides. 4. The bromo-derivatives of hydrocarbons homologous with ethylene, do not appear to form polymerides, or to be oxidised by free oxygen (Demole a. Dürr, *Ber.* xi. 1302); see also Demole (*ibid.* 1307; *Chem. Soc. J.* xxxiv. 849).

On the Imperfect Combustion and the Inflammability of Hydrocarbons, see CHEMICAL ACTION (p. 435).

On the Analysis of Volatile Petroleum Hydrocarbons by Combustion in a stream of Oxygen, see Günsberg (*Dingl. pol. J.* ccxxviii. 454; *Chem. Soc. Jour.* xxxiv. 916).

Action of Iodine Trichloride. The action of this substance on hydrocarbons, whether of the fatty or of the aromatic group, results, for the most part, in a splitting up of the molecules, and the formation of chlorinated derivatives containing smaller numbers of carbon-atoms.

Propane (or propyl chloride, b. p. 46.5°) heated with iodine trichloride to 100° – 200° in a sealed tube (which must be frequently opened to allow the escape of hydrochloric acid and then filled with chlorine-gas) is converted into perchlorethane, C^2Cl^4 , and perchloromethane, CCl^4 . Direct experiment showed that the formation of the two bodies is preceded by the formation of perchloropropane, which, under the action of chlorine, breaks up thus:

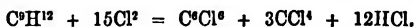


Perchloropropane is also formed by heating trichlorhydrin to 200° with iodine trichloride, as long as hydrogen chloride continues to be evolved.

Perchloropropane, heated *per se* to 300° in sealed tubes, is resolved into a mobile liquid which distils without residue between 75° and 122° , and may be separated by fractional distillation into nearly pure perchloromethane and perchlorethane: $\text{C}^3\text{Cl}^6 = \text{CCl}^4 + \text{C}^2\text{Cl}^4$. The latter when treated with iodine trichloride yields perchlorethane.

Isobutane, when heated to 210° with iodine trichloride in sealed tubes, is converted into an oily body, which is resolved by fractional distillation into perchloromethane and perchloropropane, with a little perchlorethane.

Cumene, treated with chlorine in presence of iodine, and afterwards heated to 200° with iodine trichloride in sealed tubes, is converted into perchloromethane and perchlorobenzene:



Cymene, treated in the same manner as cumene, yields perchlorobenzene, perchloromethane, and perchlorethane, the last product and half of the second being evidently formed by the breaking up of the propyl-group in cymene.

Perchlorobenzene is not affected by prolonged heating to 300° with iodine trichloride; neither are diphenylethane, anthracene, and phenanthrene broken up by like treatment (Kraft a. Merz, *Ber.* viii. 1045, 1296).

Aromatic hydrocarbons and their derivatives, subjected to *exhaustive chlorination* with chlorine containing iodine, are for the most part converted into perchlorobenzene, C^6Cl^6 , together with hydrochloric acid and various secondary products. G. Ruoff (*Ber.* 1048, 1483) subjects the compound, either in the free state or in solution, to a stream of chlorine, at first at the ordinary temperature, and with addition of a little iodine, then to the temperature of an oil bath sometimes as high as 200° , and finally heats it with excess of iodine trichloride in a sealed tube, the temperature being gradually raised from 100° to 350° , and the tube, after several hours' heating, opened from time to time in order to reconvert the liberated iodine into trichloride, and the heating then continued at 350° , till no more gas escapes on opening the tube. The final product is freed from iodine chloride by treatment with soda-ley and careful washing, and then further purified.

Diphenyl-methane thus treated is converted into perchlorobenzene and perchloromethane; *diphenyl-trichlorethane* into perchlorobenzene and perchlorethane. *Anthracene* and *phenanthrene* yield C^6Cl^6 and perchloromethane; *turpentine-oil* dissolved in 5 vol.

chloroform yields C^6Cl^6 , perchloromethane, and perchlorethane. *Diphenyl* is converted into perchlorodiphenyl, $C^{12}Cl^{10}$, which undergoes no further alteration. *Azobenzene*, *aniline* and *diphenylamine* yield C^6Cl^6 , probably with free nitrogen. *Triphenylamine* yields C^6Cl^6 and perchlorotriphenylamine, $(C^6Cl^3)^3N$, probably according to the equations, $(C^6H^3)^3N + 15Cl^2 = (C^6Cl^3)^3N + 15HCl$, and $2(C^6Cl^3)^3N + 3Cl^2 = 6C^6Cl^6 + N^2$. *Phenol*, *cresol*, *thymol*, and *resorcin* yield C^6Cl^6 , together with CO^2 , and respectively, CCl^4 and C^2Cl^4 ; CCl^4 , CCl^4 and C^2Cl^4 ; CCl^4 . *Anisöl* yields C^6Cl^6 , CO^2 and CCl^4 ; *phenetöl* yields C^6Cl^6 , CO^2 , and C^2Cl^4 . *Tetrachloroquinone* (chloranil) yields CO^2 , CCl^4 , and C^2Cl^4 . *Camphor* is converted into CCl^4 , C^2Cl^4 , and C^6Cl^6 , probably together with CO^2 . *Pyrogallol*, $C^6H^3O^3$, is the only compound which, when subjected to exhaustive chlorination, does not yield perchlorobenzene, but only perchlorethane and a small quantity of perchloromethane.

As carriers of chlorine, antimony pentachloride and molybdenum pentachloride are in many instances more effective than iodine trichloride. Respecting the latter, see Aronheim (*Ber.* viii. 1400).

On the Action of Metallic Chlorides on Aromatic Hydrocarbons at high temperatures, see also DIPHENYL (p. 658), NAPHTHALENE and TOLUENE.

Bromination. The bromination of aromatic hydrocarbons is effected by means of bromine containing iodine, in a manner similar to that described by Ruoff for effecting the chlorination. *Benzene* thus treated is converted into perbromobenzene; *toluene* into the same compound together with perbromomethane; *naphthalene* into $C^{10}H^2Br^6$ (*E. Gessner, Ber.* ix. 1555).

Conversion of the Hydrocarbons of the series C^nH^{2n} into the corresponding Alcohols. A general method of effecting this conversion by means of water or dilute acids is given by Butlerow (*Liebig's Annalen*, clxxx. 245). *Heptylene* from pentamethylethol (p. 1026), heated in a sealed tube with water, a small quantity of nitric acid, and ethyl alcohol, is reconverted into pentamethylethol. Liquid *isobutylene*, $(CH^3)^3C=CH^2$ (p. 362), similarly treated, yields trimethyl carbinol. This last transformation may also be effected by heating the isobutylene with water and a few drops of sulphuric acid to 100° . By proceeding in this way, the greater part of the hydrocarbon is converted into trimethyl carbinol, whereas isobutylene heated to 100° with a mixture of equal parts of strong sulphuric acid and water is converted into di-isobutylene. *Pseudobutylene*, $CH^3.CH=CH.CH^3$, reacts with sulphuric acid in the same manner as isobutylene.

Formation of Hydrocarbons of the Acetylene series from Aldehydes and Ketones. G. Bruylants (*Ber.* viii. 406) describes a general method of obtaining the hydrocarbons homologous with acetylene from the corresponding aldehydes and ketones, by converting these bodies into chlorides (containing the groups $CHCl^2$ and CCl^2 respectively)—by the action of phosphorus pentachloride—and dechlorinating these chlorides by means of potassium hydroxide. The aldehydes may also be treated with PBr^3 , and the products, which contain the group $CHBr^2$, debrominated with potash.

Ethylacetylene, $CH^3.CH^2.C\equiv CH$, obtained by treating methyl-ethyl ketone with PCl^3 and the product with alcoholic potash, is regarded by Bruylants as identical with crotonylene (b. p. $20^\circ-24^\circ$), although the brominated derivatives of the two exhibit different properties (compare 2nd Suppl. 401). Ethylacetylene dibromide, $C^4H^4Br^2$, is liquid; the tetrabromide, $C^4H^4Br^4$, is a solid crystalline body soluble in alcohol, ether, and carbon disulphide, subliming without previous fusion at 105° , and volatilising with vapour of water.

Orthopropylacetylene, $CH^3.CH^2.CH^2.C\equiv CH$, from methylpropyl ketone, is a mobile, colourless, alliacious liquid, boiling at $48^\circ-49^\circ$. The silver compound, C^5H^5Ag , is a white, the copper compound, $C^5H^5Cu.H^2O$, a yellow powder; both decompose readily in contact with the air. As intermediate products in the action of PCl^3 on methyl-propyl ketone are obtained a pentylene chloride, $C^5H^{10}Cl^2$ (b. p. $145^\circ-147^\circ$), and a monochloropentylene (b. p. $95^\circ-97^\circ$) (see PENTYLENES).

Isopropylacetylene, $(CH^3)^2CH.C\equiv CH$, prepared in this manner from valeraldehyde, is a very mobile liquid having an alliacious odour, a sp. gr. = 0.652 at 11° , and boiling at 37° . It forms a dibromide boiling, with decomposition, at 175° , and a tetrabromide. On the intermediate products obtained in the preparation of this compound, see PENTYLENES.

Heptene, $CH^{30}.CH^2.CH^2.CH^2.C\equiv CH$ (so-called α -naphthylidene, p. 1021), is obtained by the action of PCl^3 or PBr^3 on α -naphthaldehyde.

HYDROCAROTIN, $C^{30}H^{50}O$. This substance, which Husemann obtained, together with carotin, from the root of the carrot (iii. 190), exists also, according to Brimmer (*N. Rep. Pharm.* xxiv. 641) in angelica root, being identical with the so-called angelicin (i. 293).

HYDROCARPOL, $C^{16}H^{20}O$. A phenolic compound obtained, together with others, by the dry distillation of podocarpic acid (*q.v.*) or its calcium salt.

HYDROCASTORITE. A new mineral, occurring as a mealy deposit on kernels of castor, and exhibiting under the microscope the appearance of an aggregate of slender needles. Hardness = 2. Sp. gr. = 2.16. Colour white. Doubly refractive in polarised light. Chemical composition:

SiO_2	Al_2O_3	CaO	H_2O
59.59	21.35	4.38	14.66 = 99.98.

It is undoubtedly a product of the decomposition of castor, and is found, in company with black and red tourmaline, beryl, castor, and pollux, in veins of granite at San Pierp, Elba (G. Grattarola, *Jahrb. f. Min.* 1877, 411).

HYDROCHRYSAMIDE, $C^{14}H^{14}(NH^2)^2O^4$. See **CHRYSAMIC ACID** (p. 462).

HYDROCHLOROXYCITRACONIC ACID, $C^8H^7ClO^4$. See **CITRACONIC ACID** (oxy-) (p. 516).

HYDROCINCHONINES. See **CINCHONA-BASES** (p. 480).

HYDROCINNAMIC ACID, $C^9H^{10}O^2 = C^6H^5.CH^2.CH^2.COOH$. The benzylic ether of this acid, $C^9H^9O^2.CH^2(C^6H^5)$, is obtained by adding sodium (12 pts.) in thin slices to benzyl acetate (300 pts.), and heating the liquid till all the sodium has disappeared:

$2(CH^3.COO.CH^2.C^6H^5) + Na = CH^3COONa + H + C^6H^5.CH^2.CH^2.COO(CH^2.C^6H^5)$. At 120° the action is rapid and attended with evolution of hydrogen. When it is completed, the mass is to be thrown into water, whereupon the benzylic ether separates as a light oil, which may be dissolved in ether and purified by rectification. It boils without decomposition at a temperature above 300° , and yields hydrocinnamic acid by saponification (Conrad a. Hodgkinson, *Ber.* x. 254).

HYDROCITRIC ACID (so-called). See **CITRIC ACID** (p. 509).

HYDROCERULIGNONE, $C^{16}H^{18}O^6$. On the substitution-derivatives of this compound, see *2nd Suppl.* 377, and this Supplement, p. 549.

HYDROCOTARNINE. See **NARCOTINE**.

HYDROCYANIC ACID. See **CYANIDE OF HYDROGEN** (p. 610).

On the estimation of Hydrogen Cyanide in pharmaceutical prussic acid by means of silver nitrate and ammonium thiocyanate, see *Chem. Soc. Jour.* xxxiv. 749.

HYDROCYANOROSOLIC ACID. See **ROSANILINE**.

HYDRODIAZOBENZOIC or **HYDRAZIBENZOIC ACID**, $C^7H^8N^2O^2 = NH^2.NH.C^6H^4.CO^2H$. See **BENZOIC ACIDS**, **DIAZO-** (p. 275).

HYDRODIAZOPHENYLENE, $C^{12}H^{10}N^2$, is a green base produced by the action of stannous chloride on hydro-azophenylene hydrochloride, $C^{12}H^9N^2.HCl$, or by that of hydrogen sulphide on azophenylene mercuronitrate, $C^{12}H^9N^2.Hg(NO^3)^2$ (p. 139). Its hydrochloride crystallises in green laminae (Claus a. Hensinger, *Ber.* viii. 600).

HYDRODIBROM- and **HYDRODICHLO-OXYLEPIDENE**. See **LEPIDENE**.

HYDRODIMETHYLCAFFEIC ACID, syn. with Methylferulic acid. See **VANILLIN-DERIVATIVES**.

HYDRO-ETHYL-CEDRETE, $C^{20}H^{26}O^4$. See **PYROGALLIC ETHERS**.

HYDROFERULIC ACID,



is formed by the action of reducing agents on ferulic acid (p. 785). It crystallises from aqueous solution in microscopic plates, melts at 89° – 90° , and dissolves very easily in alcohol, ether, and hot water. It forms acid salts in which only the hydrogen of the group CO^2H is replaced by a metal, and basic salts in which the hydroxylic hydrogen is likewise replaced. The hydroferulates of the alkalis and alkaline earths are easily soluble in water. In a solution of hydroferulic acid neutralised with ammonia, silver nitrate produces a white precipitate which quickly blackens when heated; lead acetate, a white precipitate; copper sulphate throws down from very strong solutions a bluish-white salt which dissolves in excess of ammonia with blue colour. This last reaction distinguishes hydroferulic from ferulic acid, which gives with copper sulphate a dingy green precipitate, dissolving in ammonia with green colour (Tiemann a. Nagai, *Ber.* xi. 650).

HYDROFURONIC ACID, $C^7H^{10}O^3$. See FURONIC ACID (p. 834).

HYDROGEN. *Formation, Preparation, Purification.*—Selmi (*Ber.* vii. 80) observes that hydrogen is evolved during the growth of fungi, and that arsenic, antimony and sulphur may be thereby converted into their respective hydrogen compounds; he likewise attributes to this cause the formation of hydrogen arsenide from carpets, &c., containing arsenical dyes. The hydrogen thus evolved also converts potassium nitrate, first into nitrite, then into ammonia. Nitrogen in contact with fungi, decaying wood, &c., appears also to be converted into ammonia.

According to E. Schobig (*J. pr. Chem.* [2], xiv. 289) hydrogen may be freed from its compounds with phosphorus, arsenic, and antimony by passing it through a saturated neutral or acid solution of permanganate; hydrogen sulphide, on the other hand, is not oxidised by permanganate, and must therefore be removed by subsequently passing the gas through potash- or soda-ley. Pure hydrogen is also gradually but completely oxidised by permanganate, the neutral solution acting more readily than an acid or alkaline solution.

For the preparation of hydrogen gas free from hydrogen sulphide by means of zinc and sulphuric acid, J. Löwe (*Dingl. Pol. J.* cxi. 193) recommends the addition of cupric sulphate to the dilute acid, whereby the sulphur is removed within the generating vessel, in the form of copper sulphide. A portion of the copper is at the same time precipitated by the zinc in the metallic state, and partly redissolves, colouring the liquid blue. The addition of cupric sulphate likewise accelerates the evolution of the gas [by forming a copper-zinc couple].

According to Violette (*Compt. rend.* lxxvii. 940) hydrogen gas prepared with zinc and dilute sulphuric acid, is not contaminated with hydrocarbons.

A. R. Leeds (*Amer. Chemist*, vii. 183, 186) observes that pure hydrogen burns with a scarcely visible bluish flame; but that hydrogen evolved by means of zinc and potash-solution, or dilute sulphuric acid, burns with a blue flame, due probably to the presence of zinc hydride, which is removed by washing the gas with water or dilute acids.

H. Giffard (*Monit. Scient.* [3], iii. 156) prepares hydrogen on the large scale by first reducing iron from its ores by ignition in a stream of carbon oxide, and then replacing the latter by a current of aqueous vapour. The evolution of hydrogen is accompanied by reproduction of iron oxide, which may again be reduced and used as before for the generation of hydrogen.

On the prevention of Explosions in Hydrogen-generators, see EXPLOSION (p. 768).

Physical Properties.—The absolute weight of an atom of hydrogen has been calculated by J. Annaheim (*Ber.* ix. 1151) from considerations founded on the limit of visibility of certain colouring matters in dilute solutions. If 0.0007 grm. of fuchsine ($C^{20}H^{19}N^4Cl$) be dissolved in alcohol and the solution diluted to 1 litre, each cubic centimeter of the liquid will contain 0.0000007 gram of colouring matter. Now one drop = $\frac{1}{75}$ c.c. of such a solution placed on a white surface exhibits a distinct red coloration, whence it follows that 0.00000002 gram of fuchsine is still recognisable by the naked eye. Assuming now that such a drop must contain at least one molecule of the colouring matter, it follows that the atomic weight of an atom of hydrogen must be estimated at the extremely small magnitude of 0.000000000059 gram, namely $0.00000002 \div 337.5$ (the molecular weight of fuchsine). Nearly the same result is obtained by experiments with cyanine ($C^{23}H^{35}N^2I = 526$). When 1 milligram of this substance is dissolved in a litre of liquid, each drop still visibly coloured contains 0.0000000285 gram; whence the absolute weight of the hydrogen-atom is found to be 0.000000000054 gram. Hence it follows that the absolute weight of an atom of hydrogen cannot be greater than 0.0000000005 gram.

On the Molecular Relations and Diffusion of Hydrogen; also its Friction-coefficient, Compressibility, and Deviations from the Boyle-Mariotte Law; and its Liquefaction and Solidification, see GASES (pp. 847–857).

On the Relation between the two Specific Heats of Hydrogen, see HEAT (p. 933).—*On its Heat of Combustion* (pp. 952, 962).

On the Refraction and Dispersion of Light by Hydrogen, and on its Spectrum, see LIGHT.

On Electric Polarisation by Hydrogen, see ELECTRICITY (p. 713).

On Electrolysis, with evolution of Hydrogen at both Poles (p. 711).

Combination of Hydrogen with Chlorine. When hydrogen (dried by P_2O_3) is passed over porous charcoal saturated with chlorine, a considerable quantity of hydrochloric acid is formed, even in the dark. When 50 grams of charcoal were used in the experiment, the temperature fell to -20° . Water poured upon charcoal saturated with chlorine, is decomposed, with formation of hydrochloric acid and carbon dioxide (Melsens, *Compt. rend.* lxxvi. 92).

Reduction of Silver Nitrate by Hydrogen.—Russell found that perfectly pure hydrogen reduces silver from the nitrate, most readily in concentrated solutions, and that if the solution be left for some time in contact with an atmosphere of hydrogen, crystals of silver nitrate are also formed (*2nd Suppl.* 660). According to Pellet, on the other hand (*Compt. rend.* lxxviii. 1132), a neutral solution of silver nitrate is not reduced by pure hydrogen. A solution of fused silver nitrate, however, which is somewhat alkaliq from the presence of free silver oxide, is attacked at ordinary temperatures by pure hydrogen, which reduces the free silver oxide, but on acidulating the solution with nitric acid, no precipitation takes place either at ordinary or at higher temperatures. On the other hand Russell's results have been confirmed by Beketoff (*Compt. rend.* lxxix. 1413), who finds that the quantity of silver precipitated by hydrogen from a neutral solution of the nitrate is exactly proportional to that of the hydrogen absorbed; also by A. R. Leeds (*Ber.* ix. 1456), according to whose observations the quantity of silver thrown down is nearly proportional to the time of action.

Absorption of Hydrogen by Metals. 1. By Palladium. To demonstrate the absorption of hydrogen by palladium, J. L. Smith (*Amer. Chemist*, v. 213) introduces a very thin strip of palladium foil, 1.5 cm. broad and 8 cm. long into different parts of a hydrogen flame. In the upper part, where the combustion is complete, the foil retains its form unaltered; but on bringing it into the middle, where the unburnt hydrogen impinges upon its lower surface, the foil absorbs hydrogen on that surface only, and therefore curls itself up considerably. When again placed in the upper part of the flame, it resumes its original form.

Some of the physical constants of hydrogen absorbed by palladium have been determined by J. Dewar (*N. Arch. ph. nat.* l. 207). The specific gravity was found, from the mean of eight determinations, to be 0.620. The specific heat was greater when the metal was lightly charged with hydrogen than when it was strongly charged: with palladium foil it varied between 3.93 and 5.88; with palladium in bars, between 3.79 and 5.05. The expansion-coefficient of palladium charged to the maximum with hydrogen—for which Dewar gives the formula Pd^3H^2 —was, about 0.000058 between 4° and 50° , and 0.000066 between 6° and 80° .

Development of Heat in the Absorption of Hydrogen by Platinum and Palladium.—The mode of condensation of hydrogen by platinum black differs from the mode of condensation by palladium. When the gas is brought in contact with platinum black in successive portions till complete saturation is attained, the quantity of heat evolved for equal weights of the absorbed gas is not constant, as is the case with palladium. The absorption by palladium of 1 gram of active hydrogen obtained by electrolysis of dilute sulphuric acid gave:

in the first experiment	8938 gram-degrees.
„ seventeenth experiment	9167 „

The condensation of 1 gram of ordinary gaseous hydrogen by platinum gave

in the first experiment	23075 gram-degrees.
„ fourth „	13528 „

In the latter case, then, the development of heat becomes gradually smaller (Favre, *Compt. rend.* lxxvii. 649). From further experiments (*ibid.* lxxviii. 1257–1265), Favre concludes that the absorption of hydrogen by platinum is attended with the development of 2000 heat-units for 1 gram of hydrogen, and takes place without chemical alteration, but that palladium in absorbing hydrogen undergoes an allotropic modification and forms an explosive compound.

J. Moutier (*Compt. rend.* lxxix. 1242) has calculated the quantity of heat (referred to 1 kg. hydrogen) developed in the combination of hydrogen with metals, by means of the thermodynamical formula:

$$L = 0.99432 \frac{T^2}{p} \cdot \frac{dp}{dT},$$

in which p is the dissociation-tension of the compound at the absolute temperature T , based upon the values of the dissociation-tensions determined by Troost a. Hautefeuille (*Compt. rend.* lxxviii. 968; *Ann. Chim. Phys.* [5], ii. 273). The heat of combination of hydrogen with palladium increases with the temperature between 20° and 170° ; for 20° , the calculated value of L is 4147; Favre's measurements gave 4164. The calculated value of the heat of combination of hydrogen with potassium at 330° is 9300, and that of sodium 13000 gram-degrees.

From measurements of the tension of the hydrogen evolved at high temperatures from palladium-hydrogen, Troost a. Hautefeuille conclude that Pd^2H is a definite chemical compound, but that any additional quantity of hydrogen is taken up by

simple absorption. The temperature most favourable to the formation of the compound Pd^2H is 100° ; above 130° it is no longer produced.

On the Absorption of Hydrogen by *Iron*, see *Iron* in this volume; on its Absorption by *Potassium* and *Sodium*, see *2nd Suppl.* 659.

Hydrogen, occluded by metals and by charcoal, exerts a reducing and hydrogenising action, similar to that which it exhibits in the so-called *nascent state*. Nascent hydrogen, in fact, is hydrogen set free in contact with, or in very close proximity to a metal, which very probably condenses or occludes a portion of the gas, and it may therefore be supposed that the activity of the hydrogen under these circumstances is but the consequence of its intimate association with the metal, that is to say, of its being in the occluded condition. The great reducing and hydrogenising power of the copper-zinc couple doubtless depends also on the absorption of hydrogen by the finely divided metal.

The following table exhibits the resemblances and differences of the action of hydrogen occluded by palladium, platinum, copper, and wood-charcoal, and by the copper-zinc couple.

Substances employed	Substances produced by :				
	Copper-zinc couple	Palladium-hydrogen	Platinum-hydrogen	Copper-hydrogen	Carbon-hydrogen
Potassium Chlorate, KClO_3 , aq. solution	Chloride	Chloride	Chloride	Chloride	Chloride
Potassium Nitrate, KNO_3 , aq. solution	Nitrite and Ammonia	Nitrite and Ammonia	Nitrite and Ammonia	Nitrite and Ammonia	Nil
Potassium Ferri-cyanide, K^+FeCy^- , aq. solution	Ferri-cyanide	Ferri-cyanide	Ferri-cyanide	—	Ferri-cyanide
Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, aqueous alcoholic solution	Aniline	Aniline	Azobenzene	—	—
Indigo, with weak solution of potash	White Indigo	White Indigo	—	—	—
Sulphurous acid, H_2SO_3 , aq. solution	Sulphur	H_2S	Sulphur (probably)	—	—
Arsenious Oxide, As_2O_3 , aq. solution	AsH_3	Metallic Arsenic	Metallic Arsenic	—	—

The increased energy of the hydrogen in these combinations may be attributed :

- (1). To its association with a more negative element: this explanation will apply to the carbon-combination as well as the others, since charcoal conducts electricity freely.
- (2). To a peculiar atomic aggregation of the hydrogen, the variations shown in the experiments being, perhaps, attributable to different states of atomic aggregation.
- (3). To the condensed condition of the hydrogen, the observed differences between the actions of the different combinations being attributable to variations in this respect, or to the more or less firm hold which the metal has upon the gas* (Gladstone & Tribe, *Chem. Soc. Jour.* xxxiii. 306-313).

Occluded hydrogen also resembles nascent hydrogen (evolved by electrolysis) in its action on nitric and sulphuric acids (Gladstone & Tribe, *Chem. Soc. Jour.* xxxv. 172-179).

HYDROGEN DIOXIDE, H_2O_2 . On the occurrence of this compound in the air, see *АТМОСФЕРИКИ* (p. 133). J. Clermont (*Compt. rend.* lxxx. 1591) has detected it in the juices of several plants—tobacco, vine, and various species of lettuce.

On the formation of Hydrogen Dioxide, together with Nitrate and Nitrite of Ammonia, by oxidation of ammonia, see *NITROGEN OXIDES*.

According to H. Struve (*Wien. Akad. Ber.* [2 Abth.], lxviii. 432), when a shallow basin containing a dilute solution of pyrogallol is placed in another shallow basin, and covered over with a bell-jar, and the whole is exposed to sunshine or diffused daylight, hydrogen dioxide and ammonium nitrite are formed, and may be detected in the condensed water which runs down the side of the bell-jar. If potash be added to the liquid, no hydrogen dioxide is formed, but only ammonium nitrite.

Preparation.—For preparing hydrogen dioxide in considerable quantity, the following method is given by J. Thomsen (*Ber.* vii. 73). Finely divided barium peroxide, or the commercial (so-called) hydrate, is dissolved nearly to neutralisation in dilute hydrochloric acid, and to the filtered and cooled solution, baryta-water is added in quantity sufficient to throw down the foreign oxides and silica present, and to produce a slight precipitate of hydrated barium peroxide. The solution is then filtered and mixed with concentrated baryta-water, whereby crystalline hydrated barium peroxide is thrown down, which, in the moist state, may be kept for a long time in closed vessels without decomposing. To prepare hydrogen dioxide, this moist hydrate is added with stirring to dilute sulphuric acid (not stronger than 1 pt. by weight of SO^{H^2} to 5 pts. of water), till the acid is very nearly saturated; the precipitate is then left to settle, the liquid filtered, and the remainder of the acid removed by cautious addition of dilute baryta-water. The moist peroxide of barium is very easily decomposed by sulphuric acid, but the action of the acid on the dried peroxide, or even on the effloresced hydrate, is very slow and imperfect.

According to Kingzett (*Chem. Soc. Jour.* [2], xiii. 210) the compound $\text{C}^{10}\text{H}^{14}\text{O}^4$, formed by oxidation of turpentine oil, splits up, in contact with water, into hydrogen dioxide and camphoric acid: $\text{C}^{10}\text{H}^{14}\text{O}^4 + 2\text{H}^2\text{O} = \text{H}^2\text{O}^2 + \text{C}^{10}\text{H}^{16}\text{O}^4$.

Reactions.—Ammonia is readily oxidised by hydrogen dioxide, yielding nitrous acid (Weith a. Weber, *Ber.* vii. 1745). Hydrogen dioxide in dilute aqueous solution converts drying oils into non-drying oils, without itself undergoing any alteration (Cohné, *Chem. News*. xxxiii. 133).

Detection.—A solution of titanate acid in sulphuric acid is a very delicate test for hydrogen dioxide, liquids containing the latter being coloured orange ~~and~~ yellow by the reagent, according to the quantity present (Schönn, *Dingl. pol. J.* cex. 317). *Argentammonium nitrate*, provided it is destitute of every trace of free ammonia, is also a delicate test for hydrogen dioxide (Böttger, *loc. cit.*)

HYDROISOPYROMELLITIC ACID. See MELLITIC ACID (2nd Suppl. 633).

HYDROMETHANTHRENEQUINONE. See METHANTHRENE.

HYDROMETHYL-PARAOKYPHENYLACRYLIC ACID (p. 505).

HYDROMUCONIC ACID, $\text{C}^6\text{H}^8\text{O}^4$. See MUCIC ACID (2nd Suppl. 827).

HYDRONAPHTHOQUINONE. See NAPHTHOLS.

HYDRO-OXYBENZOIC ACID, $\text{C}^7\text{H}^6\text{O}^3$. This acid, isomeric with uric acid, is obtained by oxidation of oxyvitic acid, $\text{C}^7\text{H}^8\text{O}^3$. With chromic acid the yield is small; with permanganate it is somewhat larger (10 per cent. of the acid used). The oxyvitic acid dissolved in sodium carbonate is added to a slight excess of the permanganate dissolved in 40 to 60 pts. water, and the resulting hydro-oxybenzoic acid is purified by recrystallisation from water. It forms thin colourless needles melting at 274.5° (corr.) and decomposing for the most part at a higher temperature. Its solution gives a yellow precipitate with ferric chloride. The calcium salt, $(\text{C}^7\text{H}^3\text{O}^3)^2\text{Ca} + 2\text{H}^2\text{O}$, crystallises in small slightly coloured needles, which give off their water at 160° . The silver salt, $\text{C}^7\text{H}^3\text{O}^3\text{Ag}$, is obtained by precipitation from the calcium salt, but is not quite insoluble in water. Hydro-oxybenzoic acid fused with potash is converted into benzoic acid: $\text{C}^7\text{H}^6\text{O}^3 = \text{C}^7\text{H}^6\text{O}^2 + \text{H}^2\text{O}$. Oxyvitic acid is also converted into hydro-oxybenzoic acid by oxidation with weak nitric acid; but stronger nitric acid converts it into trinitroceresol (Emmerling a. Oppenheim, *Ber.* ix. 326 and 1094).

HYDRO-OXYCAMPHORONIC ACID, $\text{C}^{10}\text{H}^{14}\text{O}^6$. This acid is formed, together with camphoric acid, $\text{C}^{10}\text{H}^{16}\text{O}^4$, and camphoronic acid, $\text{C}^9\text{H}^{12}\text{O}^3$ (pp. 375, 376), by oxidising camphor with nitric acid, and is found, together with camphoronic acid, in the mother-liquors from which the camphoric acid has crystallised out. For the method of separating it from camphoronic acid, see p. 376. It is very soluble in hot, less soluble in cold water, and separates from the hot solution on cooling in beautiful triclinic crystals melting at 164.5° . Its aqueous solutions have a strongly acid reaction, and give no precipitate with ammonia and barium chloride, a character by which it is distinguished from camphoric acid.

Three of the hydrogen-atoms in hydro-oxycamphoric acid can be replaced by metals, and it also forms mono- and dimetallic salts. The acid ammonium salt, $\text{C}^{10}\text{H}^{13}(\text{NH}^4)\text{O}^6$, crystallises in colourless needles, forming globular aggregations, and melts at 178° , solidifying after some time to a porcelain-like mass. The neutral ammonium and potassium salts crystallise well, and deliquesce on exposure to the air.

The monocalcic salt, $\text{C}^{10}\text{H}^{12}\text{CaO}^6 + 2\text{H}^2\text{O}$, is easily soluble in water, and crystallises

in silky needles concentrically grouped. The corresponding *barium salt* has been obtained only as a gummy mass.

The *tricalcic salt*, $(C^8H^{11}O^2)^2Ca^2$, has been obtained as a colourless gummy mass. The corresponding *barium salt*, $(C^8H^{11}O^2)^2Ba^2$, separates in crystalline scales, easily soluble in water.

The *tricupric salt*, $(C^8H^{11}O^2)^2Cu^2$, is obtained as a bluish-green precipitate by boiling the aqueous solution of the acid with copper acetate. When dried it forms a bluish-green powder insoluble in water.

The *triargentic salt*, $C^8H^{11}Ag^3O^6$, is a white precipitate almost insoluble in cold, but soluble in hot water.

Hydro-oxyecamphoric acid heated with bromine in sealed tubes at 120° – 125° , gives hydrobromic acid and an acid melting at 226° , having the composition $C^8H^{12}O^6$, and therefore isomeric with oxyecamphoric acid.

HYDROPARAOXYBENZOÏN, $C^{14}H^{14}O^4$. See OXYBENZALDEHYDE.

HYDROPHANE. See SILICA.

HYDROPTHALIDE. See PHTHALIDE.

HYDROPIPERIC ACID, $C^{12}H^{12}O^4$. See PIPERIC ACID.

HYDROPLATINIC CHLORIDE, $Cl^2Pt(Cl^2H)^2$. See PLATINUM.

HYDROPYROCINCHONIC ACID, $C^{16}H^{16}O^7$. See CINCHONINE (p. 485).

HYDROPYROMELLITIC ACID. See MELLITIC ACID.

HYDROQUINONE. See QUINOL.

HYDROSANTONIC ACID and **HYDROSANTONIN**. See SANTONIC ACID and SANTONIN.

HYDROSORBIC ACID. See SORBIC ACID.

HYDROSULPHOBROMOBENZALDEHYDE, $C^6H^3Br(SO^3H)(COH)$. See SULPHOBROMOBENZOIC ACID.

HYDROTITANITE. This name is given by G. König (*Jahrb. f. Min.* 1876, 774) to a soft greyish mass, formed by the transformation of the perowskite of Magnet Cove, Arkansas. It contains:

TiO^2	Fe^2O^3	MgO	CaO	H^2O	Sp. gr.
82.82	7.76	2.72	0.80	5.50 = 99.60	3.681.

HYDROTOLUQUINONE. See TOLUQUINOL.

HYDROVANILLOÏN. See VANILLOÏN.

HYDROVINIC ACID. See PYROTARTARIC and UVITIC ACIDS.

HYDROKAMIC ETHERS. See HYDROXYLAMINE (p. 1079).

HYDROXYCAPRYLIC ACID, $C^8H^{13}O^2 = C^8H^{12}.CHOH.CO^2H$ (Erlenmeyer a. Sigel, *Ber.* vii. 697, 1108; *Liebig's Annalen*, clxxvii. 102). An acid of this composition, analogous to the amidocaprylic acid already described (p. 379), is obtained as a bye-product in the preparation of the latter from *cænanthol-ammonia*, hydrocyanic acid, and hydrochloric acid, and in larger quantity by the use of *cænanthol* itself instead of the ammonia-compound. The best mode of proceeding is to mix in a well-cooled vessel equal volumes of *cænanthol* and absolute hydrocyanic acid (the aqueous acid, may also be used, but the mixture must then be left to itself for some time at 30°). The product, which should form a clear solution with fuming hydrochloric acid, is boiled with hydrochloric acid in a reflux apparatus (for 4-hour if 1.5 pts. of hydrochloric acid of sp. gr. 1.19 be used), then mixed with water. The oily layer which floats on the solution of sal-ammoniac is then dissolved in ether, and on evaporating the ether, the hydroxycaprylic acid is obtained in large plates of undeterminate form, unctuous to the touch and soft enough to be cut with a knife. It has a sour taste, cooling at first, afterwards sharp and somewhat burning. It melts at 69.5° . Heated to 120° in a sealed tube with hydrochloric acid, it is easily resolved into *cænanthol* and formic acid.

Ethyl Hydroxycaprylate, $C^8H^{13}(C^2H^5)O^2$, prepared by saturating the alcoholic solution of the acid with gaseous hydrogen chloride, is a liquid boiling at 229° – 230° (bar. 715 mm.)

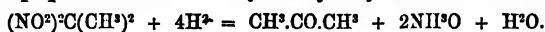
Hydroxycaprylonitril, $C^8H^{13}NO$ or $C^8H^{12}.CHOH.CN$, remains, though not quite pure, when the product obtained by heating *cænanthol* with hydrocyanic acid is evaporated on the water-bath. It is a clear colourless oil of sp. gr. 0.9048 at 17° , remains liquid at -16° and cannot be distilled either alone or with vapour of water,

beginning to split up, even at 115° , into prussic acid and cyanthol. It dissolves easily in alcohol and ether, sparingly in water. The aqueous solution gives no precipitate with silver nitrate at ordinary temperatures, but a precipitate of silver cyanide on boiling. It is decomposed by potash-solution with separation of hydrocyanic acid.

Hydroxycaprylamide, $C^8H^{17}NO^2 = C^8H^{15}.CHOH.CONH^2$, is slowly formed from the nitril by solution of sodium carbonate or by cold hydrochloric acid of sp. gr. 1.1, immediately by fuming hydrochloric acid (sp. gr. 1.19), the temperature in the latter case not being allowed to rise above 40° . The clear mixture soon solidifies to a pulp of crystals, which increase on addition of water, and may be washed with water and purified by recrystallisation from hot water. The amide thus prepared forms white laminae having a satiny lustre, melting at 150° , rather sparingly soluble in cold, somewhat more easily in hot water. It also dissolves in alcohol and in ether; and is precipitated from the alcoholic solution by water in the crystalline state.

HYDROXYLAMINE, NH^3O . *Formation*.—This compound, originally obtained by the reducing action of tin and hydrochloric acid on nitrous acid and ethyl nitrite (1st Suppl. 722), is likewise produced by means of the same reagent from the nitro-paraffins and nitrolic acids.

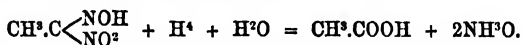
1. *Dinitropropane* is resolved thereby into hydroxylamine and acetone:



Dilute hydrochloric acid is added to the pulverised nitro-compound in a vessel fitted with a reversed condenser, and metallic tin is added, the vessel being water-cool and the mass continually shaken. On evaporating the product, hydroxylamine hydrochloride crystallises out (V. Meyer a. Locher, *Ber.* viii. 215).

2. *Dinitrobutane*, similarly treated, yields hydroxylamine, and a ketonic body, probably methyl-ethyl ketone (Meyer, *ibid.* ix. 701).

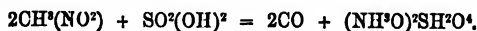
3. *Ethyl-nitrolic acid* (2nd Suppl. 894), treated with tin and hydrochloric acid, is resolved into hydroxylamine and acetic acid:



When ethyl-nitrolic acid is suddenly brought in contact with tin and strong hydrochloric acid, a violent reaction ensues, and the greater part of the nitrolic acid is decomposed, with evolution of red nitrous vapours; but by proceeding as follows, the reaction may be made to go on regularly and without violence. The solution of the nitrolic acid in the smallest possible quantity of lukewarm water is quickly cooled, and to the fine crystalline pulp thus obtained, finely granulated tin is added, and then dilute hydrochloric acid, by drops and with constant stirring, till further addition no longer produces rise of temperature, and a sample of the liquid treated with ether no longer gives up ethyl-nitrolic acid. The acetic acid produced by the reaction is easily separated by diluting the product with water and distilling, and the hydroxylamine may be obtained from the residue (Meyer a. Locher, *loc. cit.*)

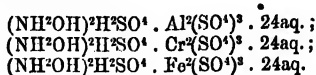
4. *Nitroform* (as ammonia-salt), treated in like manner, yielded hydroxylamine hydrochloride, hydrocyanic acid, sal-ammoniac, a small quantity of nitrogen monoxide, and a volatile substance—probably formic acid—which reduced silver-solution (Meyer a. Locher).

5. *Nitromethane*, heated with sulphuric acid, is resolved into hydroxylamine and carbon monoxide:



Equal volumes of nitromethane and fuming sulphuric acid are heated together on the sand-bath in a retort with reversed condenser till a brisk evolution of gas sets in, after which the reaction goes on spontaneously to the end, with considerable rise of temperature, so that it is necessary to mix only small quantities of the materials together at a time. The viscid products of the reaction are then heated on the water-bath till the pungent odour of sulphuric acid is no longer perceptible, then gradually added, with brisk stirring, to a mixture of alcohol and ether; and the crystalline mass which settles down is washed on a filter with the same mixture and dried under the exsiccator. If not yet quite white, it must be dissolved in water, and the solution filtered, concentrated, and mixed with alcohol, whereupon it yields snow-white shining crystals of hydroxylamine sulphate. This salt melts at 140° , and the crystals, according to measurements by Dathe, are not monoclinic as formerly stated (1st Suppl. 723), but triclinic, exhibiting the forms ∞P , ∞P_{∞} , P , $2/P_3$, P_{∞} , P_{∞} (Preibisch, *J. pr. Chem.* [2], viii. 316). It unites with aluminic, chromic, and ferric

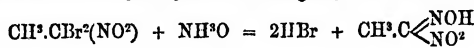
sulphates to form the following double salts, which correspond exactly in composition and crystalline form with the alums:—



A double sulphate of hydroxylamine and magnesium has also been obtained, crystallising in long needles having the composition $\text{MgSO}^4(\text{NH}^2\text{OH})^2\text{H}^2\text{SO}^4 \cdot 6\text{aq}$ (Meyerinhg, *Ber.* x. 1946).

Reactions.—Hydroxylamine reduces many metallic salts in neutral or alkaline solution, with formation of nitrogen monoxide or free nitrogen (*1st Suppl.* 723). By *Fehling's solution* in excess, it is completely oxidised to nitrogen monoxide and water: $2\text{NH}^2\text{O} + \text{O}^2 = \text{N}^2\text{O} + 3\text{H}^2\text{O}$ (*J. Donath, Ber.* x. 766). According to Lossen (*ibid.* viii. 357) it sometimes acts in the same manner also in acid solutions; *platinic chloride*, for example, is reduced when heated for some time with hydroxylamine hydrochloride. In some cases, on the other hand, it appears to act as an oxidising agent; thus *aldehyde* in contact with hydroxylamine is converted into acetic acid; and *thiocarbanilide* gently heated with it is decomposed, with precipitation of the whole of the sulphur and formation of a compound which crystallises in needles (*R. Schiff, Gazz. chim. ital.* vi. 244).

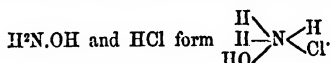
With *dibromonitroethane*, hydroxylamine forms *ethyl-nitrolic acid*:



(Meyer a. Moscher, *Ber.* vii. 1614). See NITROLIC ACIDS.

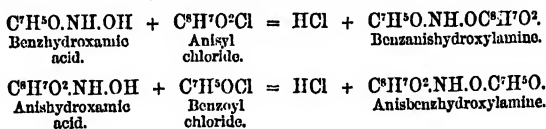
Constitution and Derivatives of Hydroxylamine.

This compound is usually represented by the formula NH^2OH , or as ammonia having one of its hydrogen-atoms replaced by hydroxyl. This view is supported by the formation of hydroxylamine by reduction of nitric acid NO^2OH , which is precisely analogous to that of organic nitro-compounds to amines; also by the behaviour of the compound to acids, which exactly resembles that of ammonia, the nitrogen, which is trivalent in the base, becoming quinquivalent in the salts; thus



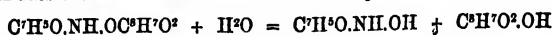
If hydroxylamine were represented by the formula $\text{H}^2\text{N}=\text{O}$, in which the nitrogen already possesses its highest combining capacity, further combination could scarcely take place.

Additional proof that hydroxylamine should be represented by a formula in which the function of at least one of the three hydrogen-atoms is different from that of the other two, is afforded by the fact, already noticed (*2nd Suppl.* 662), that benzanishydroxylamine formed by the action of amyl chloride on benzhydroxamic acid, and anisbenzhydroxylamine formed by the action of benzoyl chloride on anishydroxamic acid, are not identical but isomeric. Regarding hydroxylamine as $\text{H}^2\text{N.OH}$, the reactions just mentioned may be represented by the following equations:



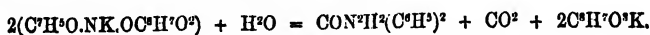
This view of the constitution of the hydroxamic acids is likewise supported by the following reactions:

1. Benzanishydroxylamine is resolved by the action of barium hydroxide into benzhydroxamic and anisic acids:



and anisbenzhydroxylamine in like manner into anishydroxamic and benzoic acids.

2. Potassium-benzanishydroxylamine is decomposed by boiling water into diphenyl-carbamide, carbon dioxide, and potassium anisate:



Potassium-anisbenzhydroxylamine, in like manner, yields potassium benzoate and dimethoxyl-phenylcarbamide :



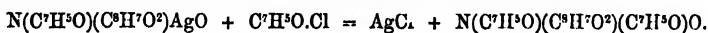
3. Benzanishydroxylamine is resolved by distillation into anisanilide $\text{NH}(\text{C}^6\text{H}^5)(\text{C}^6\text{H}^7\text{O}^2)$ and anisic acid; anisbenzhydroxylamine yields the amide $\text{NH}(\text{C}^6\text{H}^4.\text{OCH}^3)(\text{C}^7\text{H}^5\text{O})$ isomeric with anisanilide, and benzoic acid (Lossen, *Liebigs Annalen*, clxxv. 271). From further researches (*Liebigs Annalen*, clxxvi. 1-24), Lossen concludes that all the three atoms of hydrogen in hydroxylamine differ in function one from the other; inasmuch as there can exist three different tertiary derivatives, in which two of the hydrogen-atoms are replaced by benzoyl, and one by anisyl, and three others in which two hydrogen-atoms are replaced by anisyl, and one by benzoyl. Thus, distinguishing the three hydrogen-atoms by the figures 1, 2, 3, it is found that the three bodies,

Benzanishydroxylamine	$\text{N}(\overset{1}{\text{C}^1\text{H}^1\text{O}^1})(\overset{2}{\text{C}^2\text{H}^2\text{O}^2})(\overset{3}{\text{C}^3\text{H}^3\text{O}^3})\text{O}$
Dibenzanishydroxylamine	$\text{N}(\overset{1}{\text{C}^1\text{H}^1\text{O}^1})(\overset{2}{\text{C}^2\text{H}^2\text{O}^2})(\overset{3}{\text{C}^6\text{H}^7\text{O}^2})\text{O}$
Anisidibenzhydroxylamine	$\text{N}(\overset{1}{\text{C}^6\text{H}^7\text{O}^2})(\overset{2}{\text{C}^7\text{H}^5\text{O}})(\overset{3}{\text{C}^7\text{H}^5\text{O}})\text{O}$
are all different, as are also the three,	
Anisbenzanishydroxylamine	$\text{N}(\overset{1}{\text{C}^6\text{H}^7\text{O}^2})(\overset{2}{\text{C}^7\text{H}^5\text{O}})(\overset{3}{\text{C}^6\text{H}^7\text{O}^2})\text{O}$
Dianisbenzhydroxylamine	$\text{N}(\overset{1}{\text{C}^6\text{H}^7\text{O}^2})(\overset{2}{\text{C}^7\text{H}^5\text{O}})(\overset{3}{\text{C}^7\text{H}^5\text{O}})\text{O}$
Benzdianishydroxylamine	$\text{N}(\overset{1}{\text{C}^7\text{H}^5\text{O}})(\overset{2}{\text{C}^7\text{H}^5\text{O}})(\overset{3}{\text{C}^7\text{H}^5\text{O}})\text{O}.$

Moreover, each of these isomerides is capable of crystallising in different forms differing in appearance and melting point (though not in chemical reactions), so that more than one physical modification of each isomeride exists; these modifications are distinguished as α , β , γ *benzanishydroxylamine*, &c.

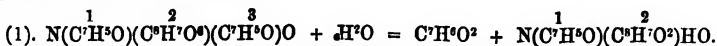
To prepare these bodies, benzoyl or anisyl chloride is made to react on the calculated quantity of the dry silver salt of the appropriate dihydroxamic acid, the materials being dissolved or suspended in benzene, and allowed to remain in contact at the ordinary temperatures until the decomposition of the silver salt is complete. The insoluble mass thus left consists of the required tri-derivative (practically insoluble in benzene) mixed with silver chloride and more or less of the dihydroxamic acid, according to the greater or lesser purity of the organic chloride used. On boiling with alcohol and cooling the filtered solution, the tri-derivative separates as an oily or semi-solid mass, soon becoming crystalline, and only sparingly soluble in cold alcohol.

(1). **Benzanishydroxylamine**, $\text{N}(\overset{1}{\text{C}^1\text{H}^1\text{O}^1})(\overset{2}{\text{C}^2\text{H}^2\text{O}^2})(\overset{3}{\text{C}^3\text{H}^3\text{O}^3})\text{O}^*$, is obtained by the action of benzoyl chloride on the silver salt of benzanishydroxamic acid, in three modifications, the reaction taking place according to the equation :



The α -modification crystallises in the triclinic system, and melts at 113° – 114° ; this is the modification formed in largest quantity: the β -variety crystallises in rhombic forms, melting at 124° – 125° , and is chiefly found in the alcoholic mother-liquors of the first crystallisation of the crude product of the reaction. The γ -modification crystallises in the monoclinic system, together with the α -crystals, and is separable only by hand-picking: it appeared to melt at 110° ; but after fusion and solidification (which required a week) it melted at 120° , indicating that by fusion it had become converted into the β -modification. In one preparation, out of 46 grams of the three modifications jointly, 35 of the α , about 6 of the β , and about 5 of the γ variety were obtained.

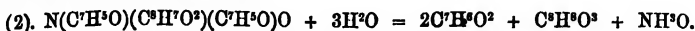
When either of these modifications is heated with dilute hydrochloric acid, decomposition is brought about in accordance with the following reaction, benzanishydroxamic acid being formed—



If, however, the acid be too strong or the action be too prolonged, more or less of the

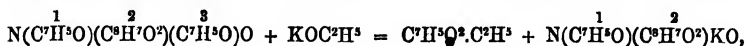
* The names of these tertiary derivatives, and the numbers placed over their formulæ, are intended to indicate nothing more than the order in which the several radicles are introduced into the hydroxylamine molecule.

product becomes split up, in accordance with the following equation, into benzoic acid, anisic acid, and hydroxylamine :



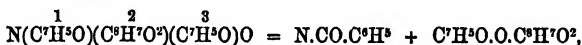
The α -modification is partially split up, and chiefly in accordance with equation (1), by heating to 100° for half an hour with 8-10 parts of hydrochloric acid of sp. gr. 1.05; the β -modification suffers no change under these circumstances; nor is more than a small quantity decomposed if the acid have a sp. gr. of 1.14; by using fuming acid, however, it is decomposed, mostly in accordance with equation (2); benzhydroxamic acid, formed in accordance with equation (1) was however separated from the products of the reaction. Modification- γ behaves as though it were a mixture of α and β , although its crystalline form negatives the supposition that such is its character; when heated with acid of sp. gr. 1.05 to 100° , it formed benzoic and benzhydroxamic acids, like the α -modification, whilst a considerable residue remained unaltered, which on examination was found to be identical with the β -variety. Nearly 40 per cent. of the β -variety was thus obtained from the γ (selected well-defined crystals being used), far too large a quantity to be due to accidental admixture from imperfect separation of the two kinds of crystals.

Similarly, alcoholic potash decomposes each of the modifications α and β in accordance with the reaction—



forming ethyl benzoate and potassium benzanishydroxamate. When aqueous caustic potash is used, the α -modification is decomposed to a considerable extent in a similar way, forming potassium benzoate and benzanishydroxamate; but a different reaction also takes place to a small extent, forming potassium anisate and dibenzhydroxamate; whilst a small quantity of substance becomes yet further decomposed, forming a mono-hydroxamic acid.

On heating the α -modification, it decomposes, with slight carbonisation, in accordance with the reaction—



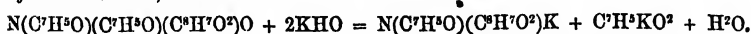
producing phenyl isocyanate and benzanisic anhydride, just as tribenzhydroxylamine forms phenyl isocyanate and benzoic anhydride; a small portion also decomposes in accordance with the reaction—



forming the isocyanate of oxymethyl-phenyl, and benzoic anhydride. Quantitative estimations of the amount of benzoic acid finally produced by first heating a weighed quantity of α -benzanisbenzhydroxylamine in a sealed tube, and then heating the products of the decomposition with strong hydrochloric acid, yielded 35.6 per cent., the first equation requiring 32.5, and the second twice as much: whence the second reaction occurs only to a very small extent.

(2). **Dibenzanishydroxylamine**, $\text{N}(\text{C}^1\text{H}^1\text{O})(\text{C}^2\text{H}^2\text{O}^2)(\text{C}^3\text{H}^3\text{O}^2)\text{O}$, is known in two modifications only, which are obtained in the manner above described by the action of anisyl chloride on silver dibenzhydroxamate. *Modification α* melts at $110-110.5^\circ$; crystals monoclinic; with hydrochloric acid of sp. gr. 1.05 it easily splits up, forming anisic and dibenzhydroxamic acids. *Modification β* melts at $109^\circ-110^\circ$; crystallises in rosettes, occurring with the last crops of crystals of α : crystalline system not determined; not attacked appreciably by hydrochloric acid of sp. gr. 1.05, but split up on prolonged heating with acid of sp. gr. 1.14, dibenzhydroxamic acid being the only dihydroxamic acid produced; most of the substance, however, was wholly split up, forming benzoic and anisic acids and hydroxylamine.

The action of potassium hydroxide on these two modifications is different from what might be expected, as, instead of the last anisyl-group being eliminated, the products formed in each instance are the potassium salts of benzoic and benzanishydroxamic acids, thus:



The silver salt of the benzanishydroxamic acid thus produced is converted by benzoyl chloride into benzanisbenzhydroxylamine.

α -Dibenzanibenzhydroxylamine is decomposed by heat exactly in the same manner as the corresponding modification of benzanisbenzhydroxylamine, the chief products

being phenyl isocyanate and benzanisic anhydride, whilst small quantities of phenyl-methenyl isocyanate and benzoic anhydride are likewise produced.

(3). **Anisidibenzhydroxylamine**, $N(C^6H^5O)(C^6H^5O)(C^6H^5O)O$, is formed by the action of benzoyl chloride on silver anisidibenzhydroxamate. The α -modification forms monoclinic crystals melting at 137° – 137.5° . It is slowly decomposed by hydrochloric acid of sp. gr. 1.05, more readily by acid of sp. gr. 1.14, forming anisidibenzhydroxamic acid; potash forms the same acid. When heated alone, it yields phenylmethoxyl isocyanate and benzoic anhydride in considerable quantity, and only small quantities of phenyl isocyanate and benzanisic anhydride, behaving in this way just conversely to the two isomerides above described.

The β -modification melts at 109.5° – 110.5° , and crystallises in small rosettes of undetermined system. It is not decomposed by hydrochloric acid of sp. gr. 1.05, and only partially attacked by acid of sp. gr. 1.14. With potash it forms anisidibenzhydroxamic acid.

By reactions exactly analogous to those above described, three metameric dianisidibenzhydroxylamines are produced, two of which form α and β modifications.

(4). **Anisidibenzhydroxylamine**, formed from anisyl chloride and silver anisidibenzhydroxamate, melts at 152° – 153° , and separates from ethereal solution in monoclinic crystals, with tabular development in the direction of the orthodiagonal. Axes, $a : b : c = 0.8662 : 1 : 0.3803$; angle $ac = 75^\circ 21.5'$. Hydrochloric acid of sp. gr. 1.05 easily decomposes it, forming anisic and anisidibenzhydroxamic acids; with potash it yields benzoic and dianisidibenzhydroxamic acids. The β -modification melts at 148° – 149° , and forms monoclinic crystals with tabular development parallel to the plane of symmetry. Axes, $a : b : c = 1.0015 : 1 : 0.7887$; angle $ac = 89.51$. This modification is formed in very small quantity only as compared with the α -modification (1 : 34).

(5). **Dianisidibenzhydroxylamine**, from silver dianisidibenzhydroxamate and benzoyl chloride, is known in one modification only. It forms monoclinic crystals melting at 147.5° ; is slowly attacked by hydrochloric acid of sp. gr. 1.05, more rapidly by stronger acid, forming benzoic acid and dianisidibenzhydroxamic acid, with no benzoylated hydroxamic acid of any kind. Caustic potash forms chiefly benzoic and dianisidibenzhydroxamic acids, together with some anisic and anisidibenzhydroxamic acids.

(6). **Benzdianisidibenzhydroxylamine** is obtained in two modifications from silver benzanisidibenzhydroxamate and anisyl chloride. The α -modification melts at 137° – 138° , and crystallises in triclinic prisms with oblique end-faces. Axes $a : b : c = 0.8025 : 1 : 0.955$; angle $bc = 99^\circ 45'$; $ac = 115^\circ 58'$; $ab = 74^\circ 43'$. Observed forms: $0P$, ∞P , ∞P , P , ∞P , $\frac{1}{2}P$. Cleavage perfect parallel to ∞P . The β -modification melts at 137.5° – 138° , and likewise forms triclinic crystals, differing however from the α -modification in the magnitudes of their angles. Axes $a : b : c = 0.4284 : 1 : 1.3997$; angle $bc = 103^\circ 7'$; $ac = 96.16$; $ab = 89.25$. Observed forms $0P$, P , P , P , P , ∞P . Cleavage perfect parallel to $0P$. Both modifications are easily decomposed by hydrochloric acid of sp. gr. 1.05 into anisic and benzanisidibenzhydroxamic acids; the α -modification also by caustic potash.

On comparing together the modes of decomposition of the above described tertiary hydroxylamines by hydrochloric acid, it is found that the radicle which is last introduced, and completes the formation of the tertiary hydroxylamine-derivative, is also the one first eliminated, the other two remaining later. The same rule applies to the action of potash, in many cases but not in all, benzanisidibenzhydroxylamine and benzdianisidibenzhydroxylamine forming partial exceptions, and dibenzanisidibenzhydroxylamine total exceptions to the rule. On the other hand, it is found that the radicle which is first introduced and forms a primary hydroxylamine derivative remains last when the tertiary derivative formed from this primary derivative is decomposed by potash in such a manner as to eliminate two out of the three radicles.

The optical examination of the crystals of the tertiary hydroxylamines—all of which exhibit strong double refraction—shows that the metameric modifications have certain optical properties in common. In benzanisidibenz- and anisidibenzhydroxylamine, the planes of the optic axes for all colours are perpendicular to the plane of symmetry; the second median lines coincide with the axis of symmetry, and horizontal dispersion takes place round the first median lines. In dibenzanisidibenz- and dianisidibenzhydroxylamine, the planes of the optic axes for all colours have the same positions, but the first median lines coincide with the axis of symmetry, and crossed dispersion takes place round this axis. There is therefore a certain correspondence between the optical and chemical characters of these bodies, indicating a connection between their physical structure and chemical properties.

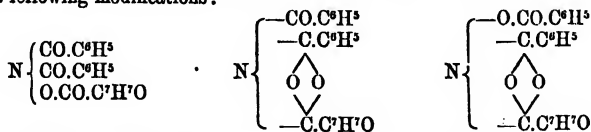
Tribenzhydroxylamine, $N(C^6H^5O)^3O$ (Lossen, *Liebig's Annalen*, clxxv. 282, 299; clxxxvi. 3, 34. O. Lehmann, *Zeitschr. f. Krystallographie*, i. 627. Klein a. Trechmann, *Liebig's Annalen*, clxxxvi. 76; *Zeitschr. Kryst.* i. 637). This compound is known in three modifications (α , β , γ), which are formed simultaneously by the action of benzoyl chloride on the potassium or silver salt of dibenzhydroxamic acid. With the former the action takes place at the temperature of the water-bath, and is completed almost instantaneously. As however the potassium salt decomposes spontaneously at this temperature, it is better to use the dry silver salt; 10 parts of this salt are drenched with 30 parts of dry benzene, and 4 pts. of benzoyl chloride diluted with 8 pts. benzene are added. The mixture, which at first forms a stiff paste, gradually separates into a precipitate and a liquid which leaves a small residue on evaporation. The precipitate, consisting of silver chloride, α and β tribenzhydroxylamine, and dibenzhydroxamic acid, is washed with ether, which takes up chiefly the α -modification, and then with boiling alcohol, which dissolves the β - and γ -compounds and the rest of the dibenzhydroxamic acid. The alcoholic solution treated with solution of sodium carbonate yields a precipitate consisting of the β - and γ -modifications, which may be purified by recrystallisation from ether or alcohol, the β -compound then separating in many-faced prisms or needles, the γ -compound (according to Steiner, *Liebig's Annalen*, clxxv. 240) in short thick crystals resembling rhombohedrons; the two kinds of crystals may be separated by hand-picking.

α Tribenzhydroxylamine melts at 100° , and is resolved by heating for an hour with hydrochloric acid of sp. gr. 1.05 into dibenzhydroxamic and benzoic acids. It is very soluble in benzene, and crystallises therefrom, also from oil [γ petroleum], and from a state of fusion, without alteration. The crystals are monoclinic, exhibiting the forms OP , $\infty P\infty$, $+P\infty$, $-P\infty$, $+2P\infty$, ∞P , $\infty P3$. Cleavage very distinct parallel to $\infty P\infty$; less distinct parallel to OP . Axes, $a:b:c = 1.856:1:1.1418$. Angle $ac = 81^\circ 42'$. Plane of the optic axes $\infty R\infty$. Double refraction strong.

β Tribenzhydroxylamine melts at 141° - 142° , and is less soluble in benzene than the preceding modification. It crystallises in the monoclinic system. Axes $a:b:c = 0.8970:1:0.3004$. Angle $ac = 23^\circ 21'$. Observed forms: ∞P , $-P$, $P\infty$, $\infty P\infty$, $\infty R\infty$. Cleavage parallel to $\infty P\infty$. Plane of optic axes $\infty R\infty$. Double refraction, positive, strong. This is the modification described in *2nd Suppl.* pp. 155, 156.

γ Tribenzhydroxylamine melts at 112° , and forms short monoclinic prisms ∞P , OP , cleavable parallel to both faces. Axes, $a:b:c = 0.9257:1:?$. Angle $ac = 65^\circ 54.5'$. Plane of optic axes, $\infty R\infty$. Double refraction strong. Dispersion slight and inclined. This modification is resolved by alcoholic potash into the ethylic ethers of benzoic and dibenzhydroxamic acids.

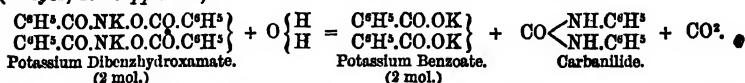
With regard to the constitution of these isomeric derivatives, it has already been observed that Lossen regards the differences between them as affording proof that the three combining capacities, or quantivalencies, of a nitrogen-atom are each different one from the other. At the same time he observes that the occurrence of three modifications of α , β , γ of a given tri-substitution derivative of hydroxylamine may be explained by difference of position of the substituted radicles; thus, anisodibenzhydroxylamine, which contains the group C^6H^5 twice and C^6H^5O once, might exhibit the three following modifications:



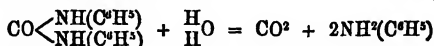
Moreover, polymerisation may be supposed to take place by the nitrogen becoming pentadic, so as to give rise to di-hydroxylamine, $\begin{matrix} HO \\ | \\ H^2 \end{matrix} N=N \begin{matrix} OH \\ | \\ H^2 \end{matrix}$; and in this, the replacement of two hydrogen-atoms by a radicle A, and of a third by another radicle B, may give rise to nine different modifications, according to the relative positions taken up by these radicles.

Hydroxamic Ethers (Lossen, *Ber.* vi. 1392; vii. 841; *Liebig's Annalen*, clxxv. 284, 313. Pieschel, *ibid.* 305. Eiseler, *ibid.* 326. Rostoski, *ibid.* clxxviii. 213. Waldstein, *ibid.* clxxxi. 384. Lossen a. Załni, *ibid.* clxxxii. 220). Lossen has shown that the di-derivatives of hydroxylamine containing two acid radicles, R, R' (which may be the same or different) may be represented by the general formula $R.NH.OR$, (p. 1075). These compounds are acids, in which the hydrogen-atom of the NH-group may be replaced by metals and alcohol-radicles, giving rise to normal salts and ethers.

Dibenzhydroxamic acid, $C^6H^5O.NH.OC^6H^5$, has been already described (2nd Suppl. pp. 154, 662). Its *potassium salt* is decomposed by water into carbon dioxide, potassium benzoate, and (not $N^3C^{10}H^{10}O$ as formerly stated, but) symmetrical diphenyl-carbamide, or carbanilide, $CO(NH.C^6H^5)^2$, identical with that which is obtained by the several reactions given in vol. i. p. 756, and by heating urea with aniline (Bacger, 1st Suppl. 398):



The proof that the diphenylcarbamide thus produced is really the symmetrical modification is afforded by the fact that when heated with strong hydrochloric acid to 180° , it is resolved into CO^2 and aniline:



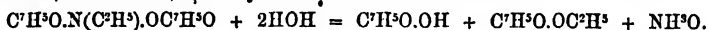
(Lossen, Ber. vii. 841).

These results have been confirmed by Rotermund (*Liebig's Annalen*, clxxv. 257), who also finds that the reaction is the same with hot and with cold water; 1 mol. dibenzhydroxamic acid and 1 mol. NaHO form diphenylcarbamide; with 2 mols. NaHO the products are benzoic and benzhydroxamic acids.

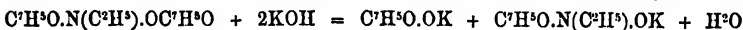
Dibenzhydroxamic acid is resolved by distillation into carbon dioxide, phenyl isocyanate (and isocyanurate), benzoic acid, and benzanilide (Pieschel):



Ethyl Dibenzhydroxamate, $C^6H^5O.N(C^2H^5).OC^2H^5$ (Eiseler, *loc. cit.*)—This ether is formed, together with other products, by the action of ethyl iodide on an ethereal solution of potassium dibenzhydroxamate. It crystallises in prisms melting at 58° , dissolves easily in alcohol and ether, and decomposes with violence at high temperatures. Heated with strong hydrochloric acid it yields hydroxylamine hydrochloride, benzoic acid, and ethyl benzoate:

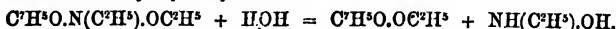


Hot potash-solution converts it into benzoate and ethylbenzhydroxamate of potassium:

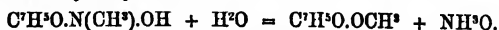


Ethylbenzhydroxamic acid, $C^6H^5O.N(C^2H^5).OH$, separated from the latter salt, is, according to Eiseler, an oily liquid. Lossen & Zanni, however, by commencing the preparation with pure ethyldibenzhydroxamate, have obtained this acid in limpid shining tables or prisms melting at 53.5° to 54.5° . It dissolves in water, alcohol, and ether. The solution of its potassium salt forms precipitates with metallic salts. By heating with hydrochloric acid it is resolved into ethyl benzoate and hydroxylamine hydrochloride (Eiseler).

Its *ethylic ether*, $C^6H^5O.N(C^2H^5).OC^2H^5$, formed by the action of ethyl iodide on ethylbenzhydroxamic acid dissolved in alcoholic potash, is a yellowish, aromatic, highly refractive liquid, insoluble in water, easily soluble in alcohol and ether. Dissolved in weak spirit and heated with a little hydrochloric acid, it is resolved into ethyl benzoate and ethyl-hydroxylamine:

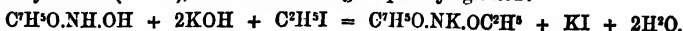


Methyl Dibenzhydroxamate, $C^6H^5O.N(CH^3).OC^2H^5$, formed like the ethyl-compound, is an oily liquid which solidifies at -15° . Potash converts it into methylbenzhydroxamic acid, $C^6H^5O.N(CH^3).OH$, which is resolved by hydrochloric acid into methyl benzoate and hydroxylamine:



Ethylene Dibenzhydroxamate, $C^6H^5[N(C^6H^5O)(OC^6H^5O)]^2$, crystallises in prisms, melts at 148° , is sparingly soluble in cold ether and alcohol, and moderately stable towards potash (Eiseler).

Ethyl Benzhydroxamate, $C^6H^5O.NH.OC^2H^5$, metameric with ethylbenzhydroxamic acid, is formed when benzhydroxamic acid (1 mol.) is left in contact for twenty-four hours with a highly concentrated solution of potassium hydroxide (2 mol.) and ethyl iodide (1 mol.), the mixture being frequently agitated:



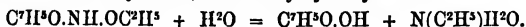
The resulting solution is freed by filtration from potassium iodide, and carbon dioxide is passed through it for about an hour, whereupon the ethylic benzhydroxamate either

separates as an oil or remains dissolved, according to the degree of dilution of the liquid. In either case it is extracted by agitation with ether, and the ethereal solution, after drying with potassium carbonate, is left to evaporate. The residual mixture of an oil and a crystalline mass is pressed, and the crystals are purified by repeated crystallisation from alcohol.

The crystals thus obtained have a tabular habit, and appear to belong to the rhombic system. They have a faint aromatic odour, melt at 64° – 65° , dissolve easily in ether and in alcohol, less easily in water. The largest crystals, which have the form of thick tablets, from predominance of the pinacoids, are obtained from the alcoholic solution; the ethereal solution yields by spontaneous evaporation flat needles or concentrically radiate crystalline masses. Benzene, added to the ethereal solution, throws down the ethylic benzhydroxamate in the form of an oil.

This compound, like its isomeride, exhibits slightly acid properties. A molecule of it is dissolved by 1 mol. potassium hydroxide, and the resulting solution gives precipitates with silver, mercury, and lead salts. The silver salt, $(C^7H^5O)NAg.OC^2H^3$, is a white precipitate easily decomposed by heat (Waldstein).

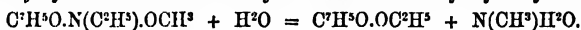
This ether, heated in a sealed tube with excess of hydrochloric acid, is resolved into benzoic acid and the hydrochloride of ethylhydroxylamine:



The latter compound is produced in like manner, together with ethyl benzoate, from the ethylic ether of ethylbenzhydroxamic acid (p. 1080).

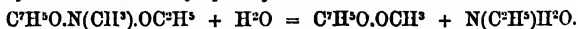
Ethylhydroxylamine hydrochloride, $N(C^2H^3)H^2O.HCl$, is a crystalline substance which deliquesces in the air and dissolves easily in absolute alcohol. It is precipitated from its alcoholic solution, on addition of ether, in large pearly laminae. When heated it melts and decomposes, evolving gas. Its solutions exhibit many of the reactions of hydroxylamine, reducing silver, mercury, and copper salts, and also chromic acid in alkaline solution. The *platinohydrochloride*, $2[N(C^2H^3)H^2O.HCl].PtCl_4$, formed by mixing alcoholic solutions of the hydrochloride and platinum tetrachloride, is deposited as a yellow crystalline powder on adding ether to the solution. It dissolves easily in water and absolute alcohol, and crystallises therefrom in prisms on evaporation (Lossen a. Zanni.—Waldstein).

Methylic Ethylbenzhydroxamate, $C^7H^5O.N(C^2H^3).OCH^3$, is prepared, like the corresponding ethylic ether, by the action of methyl iodide on ethylbenzhydroxamic acid dissolved in alcoholic potash (Lossen a. Zanni), or on the silver derivative of ethylic benzhydroxamate (Waldstein). It closely resembles its ethylic analogue, and is resolved by hydrochloric acid into ethyl benzoate and methyl-hydroxylamine:



Methylhydroxylamine hydrochloride, $N(CH^3)H^2O.HCl$, formed in the reaction just mentioned, closely resembles the ethyl-compound. It crystallises from a hot saturated solution in alcohol in flat prisms. The *chloroplatinate*, $2N(CH^3)H^2O.HCl.PtCl_4$, dissolves very easily in water and alcohol. It is precipitated from its alcoholic solution by ether as a crystalline powder, and is deposited from its solutions on evaporation in large flat orange-red prisms or tables.

Ethylic methylbenzhydroxamate, $C^7H^5O.N(CH^3).OC^2H^3$, prepared by the action of ethyl iodide on methylbenzhydroxamic acid dissolved in alcoholic potash, is a mobile liquid having an agreeable aromatic odour; when decomposed by hydrochloric acid, it yields methyl benzoate and ethylhydroxylamine:

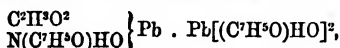


Anis- and Dianishydroxamic Acids (Lossen, *Liebig's Annalen*, clxxv. 284). These acids are produced by the action of anisyl chloride on an alkaline solution of hydroxylamine hydrochloride. From the crude product, water extracts anishydroxamic acid and a small quantity of anisic acid, the rest of the latter, together with the dianishydroxamic acid, remaining undissolved. The first two acids may be separated, either by conversion into barium salts (the anishydroxamate being insoluble in water) or directly by means of ether, which dissolves the anisic acid with only a very small quantity of the anishydroxamic acid.

Anishydroxamic acid crystallises from boiling water in colourless laminae, which easily acquire a reddish tint from the presence of slight impurities. Its normal melting point is 156° – 157° , but it melts between 140° and 150° when kept for some hours at that temperature. It dissolves readily in alcohol, is nearly insoluble in ether, quite insoluble in benzene. Its solutions, even when slightly acid, produce a deep violet colour with ferric chloride. Its acid potassium salt, $N(C^8H^7O^2)HKO.N(C^8H^7O^2)H^2O$, is somewhat sparingly soluble and crystallises in flat needles (Lossen). When a solution of lead acetate is gradually added to a solution of this acid potassium salt, a

precipitate is formed which at first redissolves, but afterwards becomes permanent. A solution filtered from the precipitate formed in the first instance, was once observed, when left at rest, to deposit colourless shining needles having the same composition as the dense white precipitate, namely $\text{Pb} \left\{ \begin{array}{l} \text{C}^2\text{H}^3\text{O}^2 \\ \text{N}(\text{C}^6\text{H}^7\text{O}^2)\text{HO} \end{array} \right\}$. The crystallised salt cannot be recrystallised from water; when boiled with water it gives up a small quantity of lead and traces of anishydroxamic acid. When heated, it suddenly decomposes, with formation of acetic acid, and perhaps of amidanisoil (N. Hodges, *Liebig's Annalen*, clxxxii. 218).

An *aceto-benzhydroamate of lead*, having the composition,



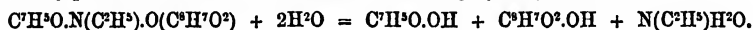
is obtained when a concentrated solution of lead acetate (6 grams to 40 c.c. H^2O) is mixed with a solution of 1 gram of potassium benzhydroxamate (Hodges).

Dianishydroxamic acid, $\text{C}^6\text{H}^7\text{O}^2.\text{NH}.\text{OC}^6\text{H}^7\text{O}^2$, crystallises in needles melting at 142° – 143° , slightly soluble in ether, insoluble in benzene. By baryta-water in excess it is resolved into anisic and anishydroxamic acids (Lossen).

Ethylic Benzanishydroxamate, $\text{C}^6\text{H}^7\text{O}.\text{N}(\text{C}^2\text{H}^3). \text{O}(\text{C}^6\text{H}^7\text{O}^2)$, is formed by the action of ethyl iodide on an ethereal solution of potassium benzanishydroxamate. It crystallises in rhombic tablets, melts at 69° , and is resolved by potash into ethylbenzhydroxamic and anisic acids:



and by potash into benzoic acid, anisic acid, and ethylhydroxylamino:



Ethylic Anisbenzhydroxamate, $(\text{C}^6\text{H}^7\text{O}^2)\text{N}(\text{C}^2\text{H}^3).\text{OC}^6\text{H}^7\text{O}$, prepared in like manner, crystallises in prisms; melts at 79° ; is decomposed by potash into ethylanishydroxamic and benzoic acids, and by hydrochloric acid into benzoic acid, anisic acid, and ethylhydroxylamino (Eiselex).

Cinnamhydroxamic Acid, $\text{C}^6\text{H}^7\text{O}.\text{NH}.\text{OH}$, is formed, together with dicinnamhydroxamic and cinnamic acids, by the action of cinnamyl chloride on hydroxylamine in aqueous solution. It melts at 110° , dissolves slightly in cold, more freely in hot water, easily in alcohol and ether, but is insoluble in benzene. Its solution colours ferric chloride deep violet. The *acid potassium salt*, $(\text{C}^6\text{H}^7\text{O})\text{NHOK}(\text{C}^6\text{H}^7\text{O})\text{NHOH}$, and the corresponding *sodium salt*, form easily decomposable yellow crystals. The *barium salt* is a sparingly soluble yellow crystalline powder which, when heated, gives off carbon dioxide and ammonia, and yields traces of a basic compound.

Dicinnamhydroxamic acid, $\text{C}^6\text{H}^7\text{O}.\text{NH}.\text{OC}^6\text{H}^7\text{O}$, is slightly soluble in ether, insoluble in water, and crystallises in prisms or laminae which melt at 152° , and are not dissolved by baryta-water. Its salts, when once separated from aqueous solution, are no longer soluble in water. The potassium salt is decomposed by boiling with water, and converted for the most part into cinnamate. When the acid is heated to incipient carbonisation, a resin is formed, from which small quantities of a crystalline powder, $\text{N}^2\text{C}^{17}\text{H}^{11}\text{O}^4$, melting at 290° , may be extracted (Rostoski, *Liebig's Annalen*, clxxviii. 213).

HYDROXYL-UREA, $\text{CH}^4\text{N}^2\text{O}^2 = \text{CON}^2\text{H}^3(\text{OH})$ (1st Suppl. 725). Potassium and sodium derivatives of this compound are obtained, though not pure, by mixing its alcoholic solution with a solution of potassium or sodium ethylate, whereupon colourless and often crystalline precipitates are formed, which rapidly attract moisture from the air. The potassium salt, dried in a stream of air, appeared to have the composition $\text{CH}^4\text{KN}^2\text{O}^2.\text{CH}^4\text{N}^2\text{O}^2$. A *lead salt* is obtained by adding lead acetate to an aqueous solution of the potassium salt till the precipitate redissolves; the solution then deposits small colourless crystals having the composition $(\text{C}^2\text{H}^3\text{O}^2)^2\text{Pb}.\text{CH}^4\text{N}^2\text{O}^2.\text{Pb}.\text{CH}^4\text{N}^2\text{O}^2$. A *cupric salt* is obtained by adding cupric acetate to the aqueous potassium salt, as a gummy precipitate which dries up to a shining green mass, and has nearly the composition $4\text{CH}^4\text{CuN}^2\text{O}^2.\text{C}^2\text{H}^3\text{O}^2$ (N. Hodges, *Liebig's Annalen*, clxxxii. 314).

HYDROXYMETHOXYCINNAMIC ACID,



This is the constitution of *ferulic acid*, obtained from *asafetida*, and produced synthetically by digesting sodium-vanillin with excess of acetic anhydride and sodium acetate (p. 785).

HYDURILIC ACID, $C^8H^4N^4O^8$ (Murdoch & Doebner, *Ber.* ix. 1102). The ammonium salt of this acid is formed, together with oxalic acid, carbon dioxide, and carbon monoxide, by heating air-dried crystallised alloxantin for three or four hours to 170° in a sealed tube. On acidulating the crude product with hydrochloric acid, and submitting it to fractional evaporation, hydurilic acid separates out first, and afterwards oxalic acid. When alloxantin is heated to 170° in contact with the air, the oxalic acid produced is resolved into CO , CO_2 , and water, and the hydurilic acid remains in the free state, especially if the heating be prolonged. Alloxantin heated to 170° with water does not yield hydurilic acid, inasmuch as the latter is decomposed by water at about the same temperature.

Air-dried crystallised alloxan is decomposed at 170° in the same manner as alloxantin; and experiment shows that it is not in the first instance resolved into alloxantin, parabanic acid, and carbon dioxide, but that the decomposition takes place in the manner represented by the equation:



Alloxan, heated to 170° in contact with the air, does not yield hydurilic acid, since it gives up its water of crystallisation even at this temperature, and anhydrous alloxan is not capable of yielding hydurilic acid.

When *hydrogen sulphide* is passed for several hours through a boiling aqueous solution of alloxantin, hydurilic acid is found amongst the products of reduction.

HYGROPHILITE. A green mineral resembling lithomarge, occurring in shaly nodules in the sandstones and siliceous conglomerates of Halle on the Saal, and in the coal-mine of Wettin. Hardness = 2. Sp. gr. = 2.670 at 18° . Two analyses, (1) made by dissolving the mineral in hydrochloric acid; (2) by decomposing it with sodium carbonate, gave the following results, leading to the formula $2(RO.SiO^2) + 3(Al^2O^3.2SiO^2) + 5H^2O$:

	SiO ² (%)	Al ² O ³	FeO	CaO	MgO	K ² O	Na ² O	K ² O
(1).	48.784	31.920	3.145	1.065	1.718 ⁽²⁾	5.673	1.364	9.015 = 102.684
(2).	48.061	32.193	3.383	1.241	1.718	5.673 ⁽³⁾	1.364 ⁽³⁾	9.015 = 102.648
	(1) With trace of TiO ² .		(2) Taken from No. 2.		(3) Taken from No. 1.			

Hydrophilite is distinguished from the other minerals of the pinite group by its solubility in potash and in hydrochloric acid, its property of exfoliating in water, and its low specific gravity. The air-dried and pulverised mineral is capable of absorbing 17 per cent. water. At 300° the air-dried substance gives off 4.5 per cent. H^2O , and at a bright red heat the loss of weight amounts to 8.697 per cent., which, when account is taken of the simultaneous increase of weight due to the conversion of FeO into Fe^2O^3 , is equivalent to a loss of 9.037 per cent. water. Microscopical examination showed the existence of numerous green pores, from which gas-bubbles escaped when the mineral fell to pieces in water (Laspeyres, *J. pr. Chem.* [2], vii. 287; *Chem. Soc. Jour.* 1873, 1207).

HYOSCYAMUS. In the mother-liquors of henbane (*H. niger*), from which hyoscyamine has been separated, R. Buchheim has found an amorphous alkaloid which he designates as *Sikeranine*.

On the Detection and Estimation of *Hyoscyamine*, see PLANT-BASES.

HYPERSTHENE. Des Cloizeaux (*Jahrb. f. Min.* 1874, 429) describes hypersthene crystals from a trachytit conglomerate from the Capucin (Mont Dore), agreeing exactly with the variety described by G. vom Rath as *amblystegite* (2nd Suppl. 55). They are accompanied by reddish needles of tridymite and zircon. Hypersthene has also been found, together with augite and oligoclase, in the lava of Santorin (Fouqué, *Compt. rend.* lxxxi. 220).

HYPOCHLOROUS ACID. See CHLORINE (p. 449).

HYPOGALLIC ACID. This name was given by Matthiessen & Foster to a modification of dioxybenzoic acid, $C^7H^6O^4$, which, according to their experiments, was obtained by boiling hemipinic acid with hydriodic acid (iii. 239). According to Beckett & Wright, however (*Chem. Soc. Jour.* 1876, i. 174), the product thus obtained is not a distinct acid, but a mixture of opianic and hemipinic acids, perhaps with addition of protocathechuic acid (see NARCOTINE). •

HYPONITROUS ACID. See NITROGEN, OXYGEN-ACIDS OF.

HYPOPHOSPHORIC and **HYPOPHOSPHOROUS ACIDS.** See PHOSPHORUS, OXYGEN-ACIDS OF.

HYPOSULPHUROUS ACID. See SULPHUR, OXYGEN-ACIDS OF.

HYPOXANTHINE, $C^8H^4N^4O$. *Sarcine*.—This substance is formed by the action of pancreas ferment on blood-fibrin; also, though in much smaller quantity, by the simple decay of blood-fibrin (Salomon, *Ber.* xi. 574). It is also produced, together with leucine, tyrosine, xanthine, guanine, and carnine, in the decomposition of the albuminous constituents of yeast (Schützenberger, *Bull. Soc. Chim.* [2]. xxi. 204).

I

ICACIN, $C^{16}H^{10}O$. The crystalline resin of Conima or Incense-resin (p. 555).

ICE. Large masses of ice may be gradually penetrated at ordinary temperatures, and with the exertion of only slight pressure, by the meshes of fine wire-gauze. The ice thus penetrated has a structure similar to that of the wire-gauze, and incloses small air-bubbles disposed in columns. A block of ice fixed between two boards was in like manner traversed, without being permanently divided, by a loaded pendulous wire, the plane traversed by the wire being merely marked by a turbidity arising from small bubbles of air (J. T. Bottomley, *Pogg. Ann.* cxlviii. 492).

From experiments on the plasticity of ice, F. Pfaff (*ibid.* clv. 169) infers that the slightest pressure is sufficient to displace the particles of ice, if it acts continuously, and the temperature of the ice and of the surrounding medium is near the melting point.

On the *Optical Structure* of Ice, see Bertin (*Ann. Chim. Phys.* [5], xiii. 283; *Chem. Soc. Jour.* xxxiv. 632).

IDOCRASE. This mineral occurs between Drammen and Konerud in Norway, in a very decomposed sedimentary rock, crystallised and crystalline. The rock is penetrated by numerous hollow spaces formed by the weathering of corals, and the idocrase crystals line these hollows particularly those formed by cyathophyllii. These crystals are occasionally 1 cm. in height; are always attached, and exhibit the combination $\infty P . P . \infty P \infty . 3P . 3P3 . P \infty 0P$. Smaller hollows, such as those formed by halysites, are filled with crystalline granular olivine and grass-green idocrase. Hyacinth-red garnets accompany the idocrase (Brögger, *Jahrb. f. Min.* 1876, 661).

IDRYL. This name was applied by Bödeker to a mixture of hydrocarbons obtained by the dry distillation of an Idrian quicksilver ore (iii. 242). Goldschmidt, who has lately examined this product, finds it to be a mixture of anthracene, phenanthrene, pyrene, chrysene, and fluoranthene, for the last of which he retains the name 'idryl' (see FLUORANTHENE, p. 724).

IGASURIC ACID. See 2nd Suppl. 665.

IHLEITE. An iron sulphate, occurring, together with other minerals, in the graphite of Mugrau, Bohemia. It is amorphous, occurring either globular or reniform, exhibiting in section a confused reticulated structure composed of fine lamellæ and fibres, which, however, on microscopical examination, do not appear to be crystalline. Sp. gr. 1·812. It is soluble in cold water, but on warming it to 40°, a basic ferric sulphate separates out. An analysis of samples of this mineral yielded the following results, proving the constancy of the process of formation, viz. :—

	SO ^a	FeO	Fe ² O ³	Al ² O ³	CaO	H ² O	
1876	38·2	2·1	24·5	—	—	35·5	= 100·3
	37·4		26·1	0·3	0·4	35·6	= 99·8
1876	37·2	1·4	25·6		0·3	35·3	= 99·8

Ihleite appears, therefore, to be a combination of ferrous and ferric sulphates, represented by the formula $FeSO^4 \cdot 9Fe^2S^2O^{12} + 120H^2O$. The mineral which most nearly approaches it in composition is misy, which differs, however, from it in its lower percentage of water and higher percentage of sulphuric acid. Ihleite is of course a secondary product, formed by the oxidation of iron pyrites, the largest and best specimens being always found in the impure, hard, stony graphite (Schrauf, *Jahrb. f. Min.* 1877, 252).

ILMENIUM. See NIOBIUM.

IMIDOCAPRYLIC ACID. See CAPRYLIC ACID (p. 381).

IMIDOSULPHONIC ACID, $\text{NH}^2\text{S}^2\text{O}^6 = \text{NH}(\text{SO}^2\text{OH})^2$. Berglund (*Ber.* ix. 252), by acting on sulphuric hydrochloride, $\text{Cl.SO}^2\text{OH}$, with ammonia, has obtained a crystallised compound which he regards as the triammonic salt of this acid, $\text{N}(\text{NH}^1)^3\text{S}^2\text{O}^6$ or $\text{N}(\text{NH}^1)(\text{SO}^2\text{ONH}^1)^2$, and as identical with crystallised ammonium sulphamate, $\text{NH}^2\text{SO}^2\text{ONH}^1$ (v. 476; Rose's Parasulphatammon; Jacquelin's sulphamide, *Berz. Jahresh.* xxiv. 196). His reasons for assigning to it the more complex formula above given are that only two-thirds [? three-fourths] of the nitrogen is given off by boiling with caustic alkalis, the remainder only on ignition with soda-lime,—and that numerous derivatives of the compound in question may be formed containing 2 at. S to 1 at. N.

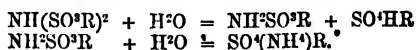
Imidosulphonic acid is, however, not bi- but tri-basic, the hydrogen-atom attached to the nitrogen being replaceable by metals, as well as those which are present in the form of hydroxyl. The acid forms, therefore, two classes of salts, viz. 'neutral salts,' $\text{NH}(\text{SO}^2\text{OR})^2$ (better called *dimetallic*), and 'basic' or *trimetallic* salts, $\text{NR}(\text{SO}^2\text{OR})^2$. All these salts are distinguished by the peculiarly close attachment of the sulphur to the nitrogen, shown, in the case of the ammonium salt, by the fact that part of the nitrogen is given off only on ignition with soda-lime, and in the case of the rest, that the sulphur is only partly removed by chloride of barium, even after prolonged boiling.

The dimetallic imidosulphonates are, for the most part, easily soluble, and only the ammonium, potassium, and barium salts are crystallisable. The *potassium salt*, $\text{NH}(\text{SO}^2\text{K})^2$, which is but sparingly soluble, is identical with Frémy's sulphammonate (v. 482), and with the disulphammonate of Claus a. Koch (*1st Suppl.* 1047), to which, however, these chemists assign the formula $\text{NH}^2\text{S}^2\text{O}^6\text{K}^2$, differing by 2 at. H from that given by Berglund. The latter regards Claus's formula as inconsistent with the formation of the ammonium salt from ammonia and sulphuric hydroxychloride, and likewise with certain reactions of amidosulphonic acid. The alteration of the formula according to Berglund's views would, however, involve corresponding alterations in those of the other sulphammonic acids described by Claus a. Koch, a point which cannot be decided without further investigation.

The trimetallic imidosulphonates are much less soluble than the dimetallic salts; they are for the most part crystalline, and are converted into dimetallic salts by treatment with weak acids. The *ammonium salt*, $(\text{NH}^1)^3\text{N}(\text{SO}^2\text{ONH}^1)^2$, agrees in composition with Rose's formula $2\text{NH}^2\text{SO}^2$. The *potassium salt*, $\text{KN}(\text{SO}^2\text{K})^2\cdot\text{H}_2\text{O}$, forms bulky crystals, probably triclinic. The *sodium salt*, $\text{NaN}(\text{SO}^2\text{Na})^2 + 12\text{H}_2\text{O}$, forms large, micaceous, very efflorescent plates. The *barium salt*, $\text{BaN}^2[(\text{SO}^2)^2\text{Ba}]^2\cdot 5\text{H}_2\text{O}$, the *strontium salt*, $\text{SrN}^2[(\text{SO}^2)^2\text{Sr}]^2\cdot 6\text{H}_2\text{O}$, and the *calcium salt*, $\text{CaN}^2[(\text{SO}^2)^2\text{Ca}]^2\cdot 6\text{H}_2\text{O}$, are obtained as slightly soluble precipitates which quickly change to masses of small needles. The *silver salt*, $\text{AgN}(\text{SO}^2\text{Ag})^2$, is a white, slightly soluble, crystalline precipitate. The *lead salt*, $\text{PbNOH}(\text{SO}^2\text{PbOH})^2$, is a white precipitate which soon becomes crystalline. When decomposed by hydrogen sulphide, it yields imidosulphonic acid, which is very unstable.

Mercurimidosulphonates, $\text{HgN}^2(\text{SO}^2\text{R})^4 = (\text{RO.SO}^2)^2\text{N.Hg.N}(\text{SO}^2\text{OR})^2$.—These salts, in which the mercury is very strongly combined, may be regarded as salts of the acid $\text{HgN}^2(\text{SO}^2\text{H})^4$, which may be obtained in the free state by decomposing the barium salt with an equivalent quantity of sulphuric acid. $\text{HgN}^2(\text{SO}^2\text{K})^4$ crystallises from hot water in thin white very stable prisms; $\text{HgN}^2(\text{SO}^2\text{Na})^4\cdot 5\text{H}_2\text{O}$ is more soluble than the potassium salt. $\text{HgN}^2(\text{SO}^2\text{K})^2(\text{SO}^2\text{Ag})^2\cdot 3\text{H}_2\text{O}$ forms long unstable needles. $\text{HgN}^2(\text{SO}^2)^4\text{Ba}^2\cdot 5\text{H}_2\text{O}$ forms microscopic needles. $\text{HgN}^2(\text{SO}^2)^4\text{Sr}^2\cdot 15\text{H}_2\text{O}$ resembles the barium salt, but is more soluble. $\text{HgN}^2(\text{SO}^2)^4\text{Mg}^2\cdot 15\text{H}_2\text{O}$ solidifies from a syrupy solution in a radiate mass. $\text{HgN}^2(\text{SO}^2)^4\text{Zn}^2\cdot 15\text{H}_2\text{O}$ resembles the magnesium salt. $\text{HgN}^2(\text{SO}^2)^4\text{Ni}^2\cdot 15\text{H}_2\text{O}$ forms emerald-green bulky prisms. $\text{HgN}^2(\text{SO}^2)^4\text{Co}^2\cdot 15\text{H}_2\text{O}$ is a red radio-crystalline mass. $\text{HgN}^2(\text{SO}^2)^4\text{Mn}^2\cdot 10\text{H}_2\text{O}$ forms hard reddish unstable crusts. $\text{HgN}^2(\text{SO}^2)^4\text{Cd}^2\cdot 12\text{H}_2\text{O}$ forms hard, unstable, very soluble crusts. $\text{HgN}^2(\text{SO}^2)^4\text{Ch}^2\cdot 15\text{H}_2\text{O}$ forms rather unstable, very soluble, bluish, warty crystals. The basic mercury salt, $\text{HgN}^2(\text{SO}^2)^4(\text{Hg}^2\text{O})^2$, forms microscopic nearly soluble crystals.

Amidosulphonic acid, $\text{NH}^2\text{SO}^2\text{H}$. The dimetallic imidosulphonates are resolved by boiling with water into acid sulphates and amidosulphonates, the latter being also partly converted into double ammonium sulphates:



The amido- and imidosulphonic acids cannot be separated by simple crystallisation, but the separation is easily effected by precipitating the imido-acid with baryta-water, in the form of a basic salt. Barium amidosulphonate is accordingly easily prepared

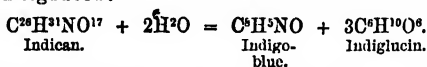
by boiling the ammonium or barium salt of the imido-acid with water, till it exhibits a strong acid reaction; then supersaturating with barium hydrate; boiling the liquid continuously till all the ammonia is driven off; filtering; removing the excess of baryta by carbon dioxide; and strongly concentrating the filtered solution, whereupon the barium amidosulphonate is deposited in long beautiful needles which have a silky lustre and are very stable (Berglund, *Ber.* 1876, 1896).

INDIAN BREAD. See LYCOPERDON.

INDICAN, $C^{12}H^{12}NO^{17}$. On the Formation and Excretion of this substance in the animal organism, see Nencki (*Ber.* vii. 1593; ix. 299; *Chem. Soc. J.* xxviii. 479); E. Salkowski (*Ber.* ix. 138; *Chem. Soc. J.* xxix. 950); Jaffé (*Chem. Centr.* 1877, 678; *Chem. Soc. J.* xxxiv. 442).

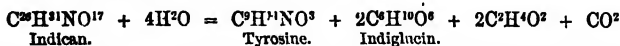
INDICATORS. On Indicators in Volumetric Analysis, see ANALYSIS (p. 83).

INDIGO. *Formation of Indigo-blue in plants.*—The formation of this substance, C^8H^6NO , from the juice of woad and other plants on exposure to the air, was formerly attributed to the oxidation of indigo-white, $C^{16}H^{12}N^2O^2$, supposed to exist in the juice in a state of solution. Schunck, however, pointed out that this could not be the case, as the sap of plants is always acid, and indigo-white dissolves only in alkaline liquids. He further showed (iii. 250) that woad (*Isatis tinctoria*) contains indican, $C^{26}H^{31}NO^{17}$, a glucoside which, when boiled with acids, splits up into indigo-blue and a saccharine substance called indiglucin:



Recently (*Manchester Memoirs*, [3], vi. 218 [1877]), Schunck has obtained indican from the leaves of *Polygonum tinctorium*, a plant used by the Chinese for the extraction of indigo, and from *Bletia Tankervillea*, an orchidaceous plant, the mode of preparation being similar to that formerly applied in the case of woad-leaves; and, lastly, indican has been detected by P. Michéa in the juice of the indigo-plant (*Indigofera tinctoria*). It may therefore be inferred that in all the plants known to yield indigo-blue, the formation of this substance is due to the decomposition of indican in the manner above mentioned. The cells of the fresh leaves of these plants do not contain any colouring matters except chlorophyll, and the conversion of indican into indigo-blue takes place only when the vitality of the cells is destroyed by cold, by organic lesions, such as the bites of insects, or by the action of chemical reagents. When the cut end of a sprig of *Polygonum tinctorium* was immersed in dilute hydrochloric acid, and the sprig was left for several days exposed to the sun and air, the acid was gradually absorbed, and passed upwards till it reached the uppermost leaves, its course being marked by a change of colour in the leaves from fresh green to dirty yellow, and afterwards to dark blue.

When an aqueous solution of indican is boiled or left to stand for some time, it undergoes a complete change, and if then decomposed by acids, yields, no longer indigo blue, but indigo-red and other products (comp. iii. 247). On one occasion an alcoholic extract of dried woad-leaves in which the indican had undergone partial decomposition by long standing, yielded, on evaporation, a quantity of a substance which exhibited all the properties of tyrosine. The formation of this body from indican may be represented by the equation:



Synthesis of Indigo-blue.—Considerable doubt appears to exist respecting the formation of this substance from liquid nitro-acetophenone, as announced by Emmerling & Engler (2nd Suppl. 666). Wichelhaus (*Ber.* ix. 1106), following the directions given by these chemists, failed to obtain it. Emmerling & Engler, on the other hand (*ibid.* 1422), maintain the correctness of their former statement, but add that, on repeating their experiments, they have not been able to reproduce the syrupy nitro-acetophenone from which the indigo-blue was obtained.

The synthesis of indigo-blue from compounds of the coal-tar group may however be effected in a different way, viz., through the medium of oxindole and isatin. Phenyl-acetic acid, $C^6H^5.CH^2.COOH$, added to fuming nitric acid warmed on a water-bath, is converted into orthonitrophenylacetic acid, $C^6H^4 \begin{smallmatrix} CH^2.COOH \\ NO^2 \end{smallmatrix}$, which by reduction yields the corresponding amidophenylacetic acid, the anhydride of which, $C^6H^4 \begin{smallmatrix} CH^2.CO \\ NH \end{smallmatrix}$, is identical with oxindole. This last compound may be converted by

the action of nitrous acid into nitrosoindole, $\text{C}^6\text{H}^4 \begin{array}{c} \text{CH(NO).CO} \\ \text{NH} \end{array}$, which by reduction yields amidoxindole, $\text{C}^6\text{H}^4 \begin{array}{c} \text{CH(NH}^2\text{)CO} \\ \text{NH} \end{array}$; this, when oxidised with ferric chloride, cupric chloride, or nitrous acid is completely converted into isatin, $\text{C}^6\text{H}^4 \begin{array}{c} \text{CO.CO} \\ \text{NH} \end{array}$; and isatin may be converted into indigo-blue by heating it with a mixture of phosphorus trichloride and pentachloride,* whereupon hydrogen chloride is given off, and isatic chloride, $\text{C}^6\text{H}^4 \begin{array}{c} \text{CO.CCl} \\ \text{N} \end{array}$, is formed, which, when reduced by heating it with phosphorus, or by treating its alcoholic solution with zinc-dust and acetic acid, yields indigo blue, $\text{C}^6\text{H}^4 \begin{array}{c} \text{CO.CH} \\ \text{N} \end{array}$ (A. Baeyer, *Ber.* xi. 582, 1228, 1296).

Reaction with Sulphur-compounds.—E. Schaer (*Ber.* ix. 340) supposes that in the action of hyposulphurous acid, hydrogen sulphide, and hydrogen persulphide on indigo-blue, colourless molecular compounds are formed from which the indigo is regenerated by all the reagents (sulphurous acid for example) which destroy these sulphur-compounds. Indigo solution is decolorised by the compounds of hydrogen persulphide with strychnine (see ALKALOIDS, p. 56).

Estimation.—A. Müller (*Amer. Chemist*, v. 128) estimates indigo-blue by the decolorising action of hyposulphurous acid. The titration of the acid with cupric sulphate, and the performance of the estimation with complete exclusion of air, are effected in the manner already explained with reference to the estimation of oxygen in blood (2nd Suppl. 200). Müller finds that 1 mol. CuSO_4 requires, to decolorise it, exactly the same quantity of hyposulphurous acid as 1 mol. of pure indigo-blue.

On the Compounds of Indigo-blue with Metallic Salts, see W. Skey (*Chem. News*, xxx. 33).

Dyeing and Printing with Indigo.—A new method of preparing an indigo-vat, founded on the rapid reduction of indigo-blue in alkaline solution to indigo-white by sodium hyposulphite, is described by Schützenberger a. De Lalande (*Bull. Soc. Chim.* [2], xx. 7). Into a solution of acid sodium sulphite of $30^\circ\text{--}35^\circ\text{Bm.}$ contained in a closed vessel, are introduced rolled strips of zinc-foil, or granulated zinc, in quantity sufficient to fill about a fourth part of the vessel, and yet to be distributed through the whole mass of liquid. After the action has gone on for about an hour, an excess of milk of lime is poured into the solution, whereby the dissolved zinc is precipitated. The filtered solution of sodium hyposulphite, Na_2SO_3 , thus obtained is mixed with ground indigo, and a sufficient quantity of lime or soda to hold the resulting indigo-white in solution.

The indigo-vat thus prepared is used cold for dyeing cotton, slightly warm for silk and wool. For printing, the above mentioned solution of indigo-white is thickened with gum and mixed with excess of sodium hyposulphite. With this colour, printing may be performed in contact with the air with the ordinary machines, the oxidation of the indigo-white being prevented by the excess of hyposulphite present. The printed cloths are hung up in the air for twelve to twenty-four hours, and when the colour has thereby been developed, they are finally washed with soap. This process, compared with the ordinary methods, is said to effect a saving of 56 to 60 per cent. of indigo.

Indigo Extract. The so-called 'Acid Extract of Indigo' is prepared by dissolving 5 pounds of Bengal indigo in 30 pounds of oil of vitriol, leaving the liquid at rest for five days, then adding 40 gallons of hot water, and filtering hot through felt. The resulting solution digested for six days with 40 pounds of common salt yields a precipitate which constitutes the acid extract. To obtain pure indigo-extract 100 lbs. of the acid extract are drenched with 12 gallons of water; the acid is immediately neutralised with soda; and the resulting precipitate collected on a filter. Bradford (*Chem. News*, xxxi. 29).

To estimate the value of such an extract, P. Hubert (*ibid.* 162) dries it at 100°

* Emmerling a. Engler obtained indigo-blue from isatin by heating the latter in a sealed tube with a mixture of phosphorus trichloride, acetyl chloride, and a little free phosphorus (2nd Suppl. 666); but, according to Baeyer, this method does not yield a satisfactory result, the product consisting chiefly of indigo-nigrin.

and incinerates it. According to Girardin, there are three sorts of extract to be distinguished, *single*, *double*, and *triple*. The mean composition of these is as follows:

	Water	Indigo	Salts
Simple Extract	89.0	4.96	5.7
Double „	85.0	10.20	4.8
Triple „	73.7	12.40	13.9

Hubert examined several such preparations made in Rheims, with the following results:

	1	2	3	4	5	6
Water	84.5	89.7	82.65	91.15	88.6	87.2
Indigo	10.6	5.6	9.55	6.05	8.2	8.4
Salts	4.7	4.7	7.80	2.85	5.2	4.4

A sure criterion of the value can however be obtained only by tinctorial experiments. For this purpose wool is dyed with a solution of 1 gram of indigo-carmin in a litre, and then more or less decolorised by a solution of permanganate containing 0.5 gram of that salt in the litre.

Indigo-red. According to observations by Nencki (*Ber.* vii. 1593), the urine of men and dogs, whose food was mixed with isatin, contained a colouring matter apparently identical with the indigo-red or urrhodin described by Heller.

Indigosulphonic Acid, $C^8H^5NO.SO^3$, or $C^8H^4NO.SO^3H$. A peculiar modification of commercial indigosulphonic acid (commonly called *indigosulphuric acid*) has been observed by S. Lupton (*Chem. News*, xxx. 215). The acid had assumed a chrome-green colour, and had deposited a purple sediment which dissolved in water with blue colour, and was not altered by sulphurous acid. The chrome-green solution, by which the violet end of the spectrum was considerably shortened, gave a dirty white precipitate with barium chloride, and was decolorised by bromine-water, and by potassium dichromate immediately, by dilute nitric acid only on boiling. Sulphurous acid instantly changed the colour of the solution to indigo-blue. The green liquid left, on evaporation, a green amorphous residue easily soluble in water and in alcohol (Berzelius' *Viridiusulphuric acid*?) A similar green coloration, accompanied by the separation of a purple precipitate, was observed on adding a few drops of a solution of potassium dichromate to a dilute solution of indigosulphonic acid mixed with hydrogen dioxide.

INDIUM. This mineral has been found by J. A. Tanner (*Chem. News*, xxx. 141) in mixtures of ore consisting mainly of calamine mixed with a considerable quantity of siliceous calamine (*Kieselzink*). A specimen from Wythe County, Virginia showed a very faint indium line; another from Leadvale, Tennessee, gave a distinct reaction. Calamine very rich in indium is found in the Onela mines in the Province of Bergamo (A. and G. de Negri, *Gazz. chim. ital.* viii. 120).

Spectrum.—Claydon a. Heycock (*Phil. Mag.* [5], i. 176), by passing the induction-spark between poles of indium, have obtained a spectrum of sixteen lines, including only the two more refrangible of the three known lines which are developed by the volatilisation of the chloride; the other fourteen lines correspond with longer durations of vibration.

Indium Platinochloride, $InCl_4.5PtCl_4 + 36H^2O$, forms honey-yellow oblique four-sided prisms, with oblique end-faces. They quickly deliquesce on exposure to the air, and give off half their water at 100° .

INDOLE, $C^8H^7N = C^8H^6 \begin{smallmatrix} \diagup CH^2.CH \\ \diagdown N \end{smallmatrix}$. *Formation and Preparation.*—1. From

Indigo. Engler a. Janceko (*Ber.* ix. 1411) confirm the statement of Baeyer (*Liebigs Annalen*, [1869], *Suppl.* vii. 56) that, in preparing indole from indigo, it is more advantageous to convert the indigo into isatin, dioxindole, and oxindole, and reduce the oxindole with zinc dust, than to treat the indigo with tin and hydrochloric acid, and subject the yellow product to the action of zinc dust (comp. 1st *Suppl.* 733).

2. From **Aniline-derivatives.** Indole is formed when ethyl-aniline, diethyl-aniline, methyl-ethyl-aniline, ethyl-acetanilide, dimethyl-*o*-toluidine, or diethyl-*o*-toluidine is passed through a red-hot tube; the first yielding only traces of indole; the second, third, and fourth, rather more; the fifth, a moderately abundant product, and the last a considerable quantity. From the brown oily liquid which collects in the receiver, the indole may be separated by means of picric acid, with which it forms a crystalline compound decomposable by ammonia. Diethyl-*o*-toluidine thus treated yields from 3 to 5 per cent. of pure indole. Diethyl-*p*-toluidine yields none (Baeyer a. Caro, *Ber.* x. 692, 1262).

3. From Albumin. Commercial albumin is mixed with water, and the finely divided pancreas of an ox (carefully freed from blood and fat) having been added, the whole is kept at a temperature of 40° to 45° for sixty to seventy hours. The liquid is then left to cool, and strained through linen. It is next acidified with acetic acid and distilled on a sand-bath till only one quarter remains. The distillate is mixed with lime-water to alkaline reaction, and shaken up with an equal volume of ether. The clear ethereal solution leaves on distillation a reddish oil with the characteristic smell of indole. This oil, when mixed with a little water, solidifies to a crystalline mass, which, on recrystallisation from pure water, yields pure indole melting at 52° (Nencki, *Ber.* viii. 336). Kühne (*ibid.* 206) likewise obtained indole by digesting albuminoids with pancreatic infusion; by distillation of decomposed pancreatic juice; and by heating dry albumin to redness with eight times its weight of potassium hydroxide. According to Engler a. Janecke (*ibid.* ix. 1411), blood-albumin and egg-albumin treated by this last method yield 0.25 per cent. casein, and gluten only 0.1 per cent.; gelatin, and creatine only traces of indole. Hence it appears that the greater the proportion of loosely combined nitrogen in the proteid, the smaller is the quantity of indole producible from it; on the other hand it was found that the residues of blood-albumin, after treatment with baryta or hydrochloric acid, yielded scarcely any indole on distillation with potash.

Properties and Reactions.—Indole (from indigo) boils with partial decomposition at 245°–246°, but volatilises completely without decomposition at 218°. Its vapour-density (determined in naphthalene-vapour, b. p. 218°) is 4.45, showing that the molecular formula is C_8H_7N (Nencki, *Ber.* viii. 1517). The indole obtained from other sources has the same vapour-density, the volumes occupied by equal weights being found by experiment to be, for indole from indigo (I), from blood-albumin (II and III), and from egg-albumin (IV),—the last three by fusion with potash—in the following ratios:

I	II	III	IV
1	: 0.995	: 0.923	: 0.908.

Nevertheless, the product obtained from albumin by fusion with potash is not identical, but isomeric, with that which is formed by reduction of indigo, or by pancreatic digestion of albuminoids, as it differs therefrom in melting point and in its behaviour with oxidising agents; for distinction therefore the product obtained by the action of melting potash on albumin is called pseudo-indole. The differences between the two modifications are as follows:

Indole melts at 52°; pseudo-indole at 85°–86° (Engler a. Janecke); 88°–89° (Kühne; probably impure). Indole from indigo suspended in water and subjected to the action of a stream of ozonised oxygen, is converted into indigo-blue, together with resinous products (Nencki, *Ber.* viii. 1517). Indole is also oxidised to indigo-blue in the animal organism, indigo-blue appearing in the urine after subcutaneous injection of indole (Nencki, *ibid.* vii. 1593). Pseudo-indole treated with ozonised oxygen as above is converted into a yellowish-brown substance having an odour different from that of indole, and not yielding any blue insoluble colouring matter when treated with ether. Indole treated with chromic acid immediately yields a bulky violet-brown precipitate, which is insoluble in ether, chloroform, and benzene, dissolves sparingly and with red colour in alcohol and aniline, easily and with violet colour in concentrated hydrochloric acid. Pseudo-indole, treated with chromic acid, gives, only in concentrated solution and after some time, a reddish-yellow precipitate, which is nearly insoluble in ether, chloroform, and benzene, but dissolves with yellow colour in aniline and in hydrochloric acid. Pseudo-indole gives with nitrous acid a precipitate, which, when treated with alkalis, does not emit the odour of indole.

Another isomeride of indole is formed, together with a non-azotised body, by the action of ammonia on chloracetyl-benzene, $C^6H^5.CO.CH^2Cl$. When this compound is boiled with aqueous ammonia for about an hour, or heated with it to 140°–150° in a sealed tube, it is converted into a deep red liquid which solidifies on cooling, whilst the whole of the chlorine remains in the aqueous solution in the form of sal-ammoniac. From this red product, ether separates two compounds, one of which remains undissolved when the red substance is digested with ether for a short time, while the other dissolves in the ether and separates slowly therefrom.

The former of these, which is formed in small quantity only (8 per cent. of the chloracetyl-benzene), is the iso-indole. It is insoluble in water, very slightly soluble at ordinary temperatures in alcohol, ether, benzene, carbon disulphide, and glacial acetic acid, and crystallises from the hot acetic acid solution, also from boiling alcohol, in serrated colourless laminæ having a silky lustre, and consisting of aggregates of broad pointed needles. It melts at 194°–195°, and sublimes in nacreous laminæ. It dissolves in strong hydrochloric acid, and separates therefrom in the crystalline state,

partially on cooling, immediately on dilution (Staedel a. Rügheimer, *Ber.* ix. 563, 1758).

Nitroso-di-indole, $C^{10}H^{12}(NO)N^2$.—This compound, commonly called *nitroso-indole*, is not known in the free state, but its nitrate, $C^{10}H^{12}(NO)N^2.NO^3H$, is obtained by adding to an aqueous solution of indole (prepared by pancreatic digestion of albumin) a few cubic centimeters of hydrochloric acid, and a large quantity of nitric acid, freed by evaporation from too great an excess of nitrous acid, and distilling the mixture. This nitrate dissolves readily, and with dark colour, in alcohol, less easily in ether, and is nearly insoluble in water acidulated with nitric acid. It decomposes when dried in a vacuum, and detonates sharply when heated. Free nitroso-di-indole has not been obtained. The *hydrochloride* forms red, amorphous, very unstable flocks (Nencki, *Ber.* viii. 1670).

Hydrazo-di-indole, $(C^8H^{10}N)^2N^2H^2 = \begin{array}{c} C^8H^{10}N-NH \\ | \\ C^8H^{10}N-NH \end{array}$, is readily formed by the

action of reducing agents, *e.g.* alcoholic ammonium sulphide, on the nitroso-compound. It dissolves in alcohol and in ether, crystallises in shining yellow needles, and melts at 140° to a deep blue mass which, at a higher temperature, gives off ammonia and chars. Hydrazo-di-indole dissolves with yellow colour in strong sulphuric acid, the solution turning red when heated. Acids and alkalis convert it into a dark-brown colouring matter, regarded by Nencki as a zoindole.

INDOLINE, $C^{10}H^{11}N^2$ (Schützenberger, *Compt. rend.* lxxxv. 147). This polymericide of indole is obtained by heating indigo-blue with 2 pts. barium hydrate, $1\frac{1}{2}$ zinc-dust, and 10 water to 180° . On exhausting the product with alcohol and evaporating, a dark-coloured resinous substance remains, brittle at ordinary temperatures, but softening even below 100° ; and on heating this resin with zinc-dust, indoline sublimes in long pale yellow shining needles. It melts at about 245° , is insoluble in water, but soluble in alcohol and ether, to which it imparts a bluish fluorescence. It possesses basic properties, and yields with acids crystallisable salts mostly insoluble in water.

The *picrate*, $C^{10}H^{11}N^2.C^6H^3(NO^2)^3O$, is slightly soluble in alcohol. Indoline dissolves in hot *hydrochloric acid*, and the solution forms with *platinic chloride* a brown granulo-crystalline precipitate. The solution of indoline in strong *sulphuric acid* exhibits a blue fluorescence, and, on exposure to the air, deposits indoline sulphate in brown crystals. Indoline is partly decomposed by sublimation, yielding crystals, some of which resemble anthracene, while others are like anthraquinone.

If the heating of indigo with baryta-solution be interrupted before the reaction is complete, the solution will be found to contain, together with indoline, a substance which, on exposure to the air, is deposited in red flocks having the composition $C^{10}H^{12}N^2O$. This body dissolves in alcohol, and separates therefrom in red crystalline granules; also in dilute hydrochloric acid, with red colour, and is precipitated by ammonia.

INK. According to R. Böttger (*N. Rep. Pharm.* xxiii. 47), an excellent black ink is obtained by triturating 1 pt. pyrogallol, 3 pts. finely pounded gum-arabic, and 3 pts. neutral ammonium vanadate, with a suitable quantity of cold rain-water.

Böttger (*Dingl. pol. J.* ccix. 176) describes an indelible ink prepared by triturating 1 dram of aniline black with a mixture of 60 drops of strong hydrochloric acid and $\frac{3}{4}$ oz. alcohol, and diluting the resulting deep blue solution with a hot solution of $1\frac{1}{2}$ drams of gum-arabic in 3 ozs. of water. This ink does not attack steel pens, and is not destroyed either by acids or by alkalis. If the solution of aniline black be diluted with a solution of $\frac{3}{4}$ oz. shellac in 3 ozs. spirits of wine, an excellent varnish is obtained for wood and metals.

Coloured Inks.—A good red ink is said to be obtained by triturating carmine with water-glass solution, and adding sufficient of that solution to make the ink run well from the pen. The ink must be protected from the air, best in a bottle closed with a cork soaked in oil. The writing dries very quickly (*Dingl. pol. J.* ccix. 316).

The following coloured inks are described by C. H. Vioud (*ibid.* ccxiv. 167). Red ink may be prepared by dissolving 1 pt. anhydrous fuchsine in 150–160 pts. boiling water, and, if the ink runs too easily, adding a solution of 3 pts. gum-arabic in 6 pts. water. Blue ink is a solution of 1 pt. anhydrous aniline blue (*bleu de nuit*) in 200–250 pts. water. Violet ink is prepared by dissolving 1 pt. blue-violet aniline in about 300 pts. water. This ink is very sensitive towards ordinary copying ink made from logwood extract; if a pen which has been used for copying ink be dipped into the violet aniline ink just mentioned, the writing immediately becomes pale and granular. Green ink is prepared by dissolving 1 pt. iodine-green in 100–110 pts. water.

Yellow ink is best prepared by dissolving 1 pt. picric acid in 120–140 pts. water. As copying inks, these inks cannot be recommended. The characters made with them are indeed soluble in water, and may therefore be transferred to damp paper; but the writing is, for the most part, not strong enough to yield a legible copy. If the strokes are made very thick, they exhibit on drying the well-known metallic lustre of the aniline dyes.

• INOSITE, $C^6H^{12}O^6$. H. Vohl, by treating this substance with strong nitric acid (sp. gr. 1.52), obtained *hexnitroinosite*, $C^6H^6(NO^2)^6O^6$ (iii. 276). Further experiments have shown that *trinitroinosite* is formed at the same time. Finely pulverised anhydrous inosite is added, with continual stirring, either to well-cooled strong nitric acid, or to a cooled mixture of 1 mol. nitric and 2 mol. strong sulphuric acid. In the latter case, the inosite is quickly converted into a sandy crystalline mass; in the former case, the same substance is precipitated on addition of sulphuric acid. By washing this product with water and dissolving it in boiling alcohol, a solution is obtained which, on cooling, deposits hexnitro-inosite in tablets and prisms; and the mother-liquor yields by spontaneous evaporation, first white concentrically grouped needles of trinitroinosite, $C^6H^6(NO^2)^3O^6$, afterwards a gummy mass, from which inosite is reproduced by the action of ammonium sulphide (*Berl. Ber.* vii. 106).

Fermentation of Inosite.—According to Hilger (*2nd Suppl.* 669), the lactic acid formed in the fermentation of inosite is ethylene-lactic (paralactic) acid; Vohl, on the other hand, finds that it is identical with ordinary lactic acid (*Ber.* ix. 984).

INSECT-POWDER. R. Rother (*Pharm. J. Trans.* [3], vi. 781) finds, in the insect-powder obtained from *Pyrethrum caucasicum*, *roseum*, &c. (1) a resinous, greenish-yellow acid, which he calls *Persicein*; (2) a light brown acid, *Persiretin*; and (3), an easily soluble acid, *Persicin*. This last, which appears to be the active principle of the powder, is a glucoside, easily split up by boiling with dilute acids into persiretin and sugar.

INSOLINIC ACID. See TEREOPHTHALIC ACID.

INVERTIN. The sugar-inverting constituent of yeast. See FERMENTS (p. 784).

INVERT-SUGAR. See SUGAR.

IODINE. *Occurrence.*—According to H. Zenger (*Arch. Pharm.* [3], vi. 137), iodine is found, together with bromine, in fresh-water plants. According to A. Guyard (*Bull. Soc. Chim.* [2], xxii. 60), the iodine sometimes present in saltpetre is in the form, not of potassium iodate, but of sodium iodate or iodide, sometimes of sodium periodate.

According to Stanford (*Dingl. pol. J.* cccxvi. 85; *Chem. Soc. Jour.* xxxiv. 169), kelp contains about 0.16 per cent. of iodine. Seaweeds possess the power of taking the iodine from the sea-water, but in different degrees, as shown in the following table; they take up ten times more iodine than bromine. 100 parts of dried algae contain:

	Sarphut	Schweitzer	Godechens	Wallace	Stanford
<i>Laminaria digitata</i>	0.135	—	0.625	0.4440	0.4535
„ <i>saccharina</i>	0.230	3.880	—	0.2880	0.2794
<i>Fucus serratus</i>	0.124	0.058	0.177	0.0565	0.0856
„ <i>nodosus</i>	—	—	0.074	0.0396	0.0572
„ <i>vesiculosus</i>	0.001	—	—	—	0.0297
<i>Zostera marina</i>	0.0005	—	—	—	0.0457
<i>Rhodomela pinnastroides</i> . .	—	—	—	—	0.0378
<i>Hyderix siliquosa</i>	—	—	—	—	0.2131
<i>Hymanthalia lorea</i>	—	—	—	—	0.0892
<i>Chordaria flagelliformis</i> . .	—	—	—	—	0.2810
<i>Cladophora glomerata</i> . . .	—	—	—	—	—

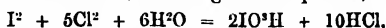
According to Sonstadt, the iodine in sea-water is in the form of calcium iodate, 1 part of which is contained in 250,000 parts of the liquid (*2nd Suppl.* 671); and since the equivalent weight of calcium iodate is $\frac{I^2O^2Ca}{2} = \frac{342}{2} = 171$, it follows that

1 pt. of iodine is contained in $250,000 \times \frac{171}{127} = 336,610$ parts of sea-water.

Preparation.—The manufacture of iodine (and bromine) from the mother-liquor of

kelp, as now practised in Glasgow,* is described by Mr. Stanford (*loc. cit.*) as follows: The liquor, having a density of 85 to 95 Twaddle, is mixed with one-seventh of its weight of oil of vitriol (145 Tw.), and left for 24 hours, whereby the sulphur-compounds contained in it are decomposed, and sulphur is precipitated. The liquor is then distilled with manganese dioxide in an iron still having a leaden cover and two arms connected with two series of stoneware cells, in which the iodine condenses in hard masses. After all the iodine has passed over, more manganese dioxide is added, the leaden arms are connected with another condensing apparatus, either of lead or earthenware, and the bromine is collected therein.

Reactions.—With Chlorine. G. Sodini (*Gazz. chim. ital.* 1876, 321), from experiments on the manner in which the action of chlorine on iodine in presence of water is affected by the quantity of the latter, finds that, to ensure the complete conversion of the iodine into iodic acid, according to the equation,



there must be at least 20 pts. of water present to 1 pt. of iodine. With a smaller quantity of water, the quantity of iodic acid formed decreases, and a corresponding amount of iodine chloride is produced; and when only the theoretical quantity of water indicated by the preceding equation is employed, scarcely a trace of iodic acid is produced.

With Ozone. According to J. Ogier (*Compt. rend.* lxxxv. 957), this reaction yields, besides iodic acid, an intermediate product having the composition I^2O^3 (p. 1095).

With Palladium Chloride and Potassium Ferrocyanide. When iodine in alcoholic solution or in fragments is added to an aqueous solution of potassium ferrocyanide, it is not precipitated on addition of palladium chloride, but the yellow colour of the liquid changes to a green, which becomes particularly bright on heating, and is due to the formation of palladium ferrocyanide. A solution of potassium ferrocyanide likewise dissolves iodine, which then also is no longer precipitated by palladium chloride. In these solutions iodine cannot be detected by means of starch; neither can it be separated from bromine and chlorine by means of palladium chloride in presence of potassium ferrocyanide (S. Kern, *Chem. News*, xxxiii. 184).

Alteration of Iodine tincture.—This tincture (alcoholic solution), when kept for some time, is found to contain hydriodic acid, the quantity of which may be determined by diluting the tincture largely with water, so as to precipitate the greater part of the iodine, then treating the filtrate with barium carbonate, and estimating the dissolved barium iodide. A tincture ten years old was found to contain 1.12 per cent. hydriodic acid (P. Carles, *Pharm. J. Trans.* [3], vi. 88).

Detection and Estimation—On the estimation of Iodine by means of soluble Thiocyanates, see HALOGENS, p. 923. On the estimation of Iodine in Organic Compounds, see p. 924; also Brügelmann (*Zeitschr. anal. Chem.* 1877, pp. 1–21; *Chem. Soc. Jour.* xxxi. 739).

For the estimation of iodine in cuprous iodide, Ulex (*Arch. Pharm.* [3], v. 524) expels the iodine by means of ferric chloride, and receives it in a solution of potassium iodide, the operation being conducted in an apparatus which allows of the aspiration of a stream of air through the liquid during the ebullition, whereby the process is greatly accelerated. Or the cuprous iodide is decomposed with zinc powder, and the soluble zinc iodide thereby produced is titrated by Mohr's method with silver solution and neutral potassium chromate.

For the exact estimation of iodine in urine, A. Hilger (*Zeitschr. anal. Chem.* 1873, 342; 1874, 476) acidulates 40 c. c. of the urine with hydrochloric acid, and determines the iodine by means of a standard solution of palladium chloride, 10 c. c. of which are equivalent to 0.00119 iodine, the strength having been determined by means of potassium iodide. The titration is best performed by measuring out 10–20 c. c. of the palladium solution, heating it on the water-bath in a flask with ground stopper, and adding the urino-solution, previously brought to a determinate volume, till the whole of the palladium is precipitated, the completion of the process being ascertained by the testing of small filtered samples. The presence of phosphates and sulphates does not interfere with the determination.

Iodides. 1. *Hydrogen Iodide* or *Hydriodic acid*.—On the Direct Formation and Dissociation of this compound, see CHEMICAL ACTION (p. 428). On its Heat of Formation, see pp. 952, 963.

Preparation.—For the preparation of gaseous hydrogen iodide, A. Bannow (*Berl. Ber.* vii. 1498) introduces red phosphorus into a tubulated retort, and adds to it, by means of a dropping funnel, a solution of 2 pts. iodine in 1 pt. hydriodic acid of sp. gr. 1.7. The evolution of gas begins without external heating, but after the whole

* The process described in vol. iii. p. 290, as practised in Glasgow, has been abandoned for many years,

of the liquid has been added, the action must be assisted by a gentle heat. The quantity of the solution must be so regulated that the phosphorus and iodine may be present in the ratio of P^2 to I^2 . If heat be applied too soon, a considerable sublimation of phosphonium iodide will take place.

Kolbe (*J. pr. Chem.* [2], xv. 172) finds that the method of preparing aqueous hydriodic acid, recommended by Vigier and copied into many text-books, which consists in pouring 15 pts. of water on 1 pt. of amorphous phosphorus, adding 20 pts. of iodine, and driving over the resulting hydriodic acid by heating [the reaction being represented by the equation $P^2 + 5I^2 + 6H^2O = P^2O^5 + 10HI$ (1st Suppl. 738)], always yields a dilute and strongly iodised acid, and that a better product is obtained by the older method of first preparing phosphorus iodide with 1 pt. amorphous phosphorus and 10 pts. iodine, and decomposing this compound with water.

The following process is recommended by W. Stevenson (*Chem. News*, xxvi. 201) for preparing hydriodic acid, iodic acid, and the greater number of iodides and iodates. 3 pts. iodine are dissolved in a solution of 2 pts. barium hydrate in 4 pts. boiling water, and the liquid, after it has become neutral and colourless, is filtered. The insoluble barium iodate thus obtained serves for the preparation of iodic acid and metallic iodates, and the soluble barium iodide for that of hydriodic acid and iodides.

On the reaction of Hydriodic acid with Ethers, see p. 741.

Carbon Iodide or Tetriodomethane, CI^4 (see p. 404).

On the Periodides and Sulphatoperiodides of the Cinchona-bases, see pp. 479, 486, 489-491, and 493.

Iodine Bromide, BrI . This, according to Bornemann, is a crystalline body having the colour of iodine; melting at 36° ; distilling with partial decomposition; subliming in fern-like groups of crystals; and dissolving in water with much less separation of iodine than that which takes place with iodine chloride. The hydrate, $BrI \cdot 5H^2O$, described by Löwig (iii. 293) does not exist.

Iodine Chloride (Bornemann, *Liebig's Annalen*, clxxxix. 184). To prepare the monochloride, ICl , chlorine was passed over iodine contained in a retort, till crystals of the trichloride made their appearance, and the red-brown liquid was distilled into glass tubes which were immediately sealed. The contents of those which contained small quantities of the trichloride solidified after a while, yielding very fine crystals of the mono- and tri-chloride, whereas those of the tubes in which there were no crystals of the trichloride did not solidify, even in a freezing mixture. When, however, they were opened, their contents solidified after a while, with the exception of those which contained free iodine as well as ICl , a result which agrees with an observation made by Breken (*Berl. Ber.* viii. 489) that the crystallisation of ICl is facilitated by ICl^3 , but retarded by free iodine. Iodine monochloride is decomposed by water, as observed by Trapp and by Schützenberger (iii. 293) with formation of iodic and hydrochloric acids and separation of iodine. The quantity of chlorine required to dissolve iodine suspended in water increases with the proportion of water present, and for the complete conversion of the iodine into iodic acid, at least 20 pts. of water must be present to 1 pt. of iodine. In more concentrated solutions the passage of chlorine is attended with the separation of iodine trichloride as well as of iodic acid.

Hydrogen-iodine Chloride, $ICl \cdot HCl$, is a yellow, volatile compound, formed, according to Schützenberger (*Compt. rend.* lxxxiv. 389), together with iodic and hydrochloric acids, by the action of water on the chloride of iodine, and may be extracted from the aqueous solution by ether. The formation of this body is the cause of the stability of iodine monochloride in water containing hydrochloric acid, observed by Gay-Lussac (iii. 293).

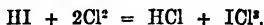
Schützenberger has also examined the action of water on various systems of iodine chlorides comprised between the limits ICl^3 and ICl . Each of these systems may be regarded as a mixture of the two components ICl^3 and ICl , the former of which is resolved by water into iodic and hydrochloric acids: $ICl^3 + 3H^2O = IO^3H + 5HCl$. If now the quantity of hydrochloric acid thus formed is equal to or greater than that which is required to convert the ICl into the compound $ICl \cdot HCl$, which is stable in water, the monochloride ICl will not be decomposed. In the contrary case, however, it will suffer decomposition just as if it were alone, that is to say, it will be resolved by the water into iodic acid, hydrochloric acid and a corresponding quantity of free iodine, till the hydrochloric acid thereby produced is sufficient to convert the rest of the monochloride into the stable compound $ICl \cdot HCl$:



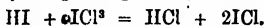
Iodine trichloride may accordingly be regarded as a compound of ICl^3 and ICl , and will give up half its iodine in the form of iodic acid. The system, $4ICl^2 = ICl^3 + 3ICl$,

will in like manner give up one-fourth of its iodine as iodic acid. The system $\text{ICl}^{\circ} \cdot 5\text{ICl}$ is the most highly iodised system that can be decomposed without separation of iodine.

Trichloride, ICl° .—Christomanos (*Berl. Ber.* x. 434) prepares this compound by the action of chlorine on hydrogen-iodide:



Pure hydrogen iodide, obtained by gradually adding iodine to a mixture of amorphous phosphorus with a few drops of water gently heated in a retort, is passed through a calcium chloride drying-tube into a tall cylinder or flask filled with dry chlorine. At the first contact of the two gases, a dense white cloud of hydrogen chloride is formed, in which float innumerable golden-yellow spangles of iodine trichloride. When the hydrogen iodide is in excess, the fumes have a reddish-violet colour, and the spangles of trichloride then assume a still more brilliant appearance. Generally, if the two gases are tolerably pure, the hydrogen iodide takes fire in the chlorine. Violet fumes of iodine are then set free, which immediately combine with chlorine to form brilliant golden-yellow crystals of trichloride, whilst the hydrogen burns with bright red-flame in the iodine vapour. The sides of the cylinder speedily become covered with yellow crystalline scales of the trichloride. If after this the current of hydrogen iodide be continued, the crystals assume a darker colour, becoming orange and brown, and finally deliquescent, owing to the following reaction:—



The process forms a very striking lecture experiment.

Iodine trichloride is a lemon- to orange-yellow solid, very easily decomposable. It can be preserved only in an atmosphere of chlorine. In the air it volatilises perceptibly, even at -12° . It is less volatile in carbon dioxide, especially when cooled to -12° , but it still loses weight distinctly, and at the same time an odour of carbonyl chloride, COCl^2 , is perceptible. When heated to 100° in an open glass tube it is instantly decomposed into free chlorine and iodine monochloride, which latter boils rapidly at that temperature. In an atmosphere of chlorine the trichloride melts at 33° . It dissolves in water. Strong sulphuric acid throws down from the concentrated aqueous solution a yellow powder; but the same acid dissolves the trichloride with yellow colour. The trichloride dissolves in potash, forming iodide, chloride, iodate, and chlorate. In an atmosphere containing ammonia it emits dense white fumes. An excess of ammonia immediately converts it into nitrogen iodide, sal-ammoniac, and ammonium iodide. The trichloride dissolves in benzene with dark cherry-red colour. It is immediately decomposed by carbon bisulphide, sulphur chloride being formed. It oxidises solutions of sulphur dioxide and ferrous sulphate when boiled therewith. Potassium and phosphorus take fire in contact with it. The trichloride volatilises in a current of hydrogen in the cold without acting upon it; but on gentle heating, hydrogen chloride and liquid iodine monochloride are formed.

With regard to the melting point, Lothar-Meyer (*Ber.* x. 648) observes that the fusion of iodine trichloride is merely a consequence of its dissociation, which depends upon pressure, presence of chlorine, &c., so that the melting point 33° observed by Christomanos must have been determined by accidental conditions. The beginning of the decomposition may take place, according to circumstances, at 25° or above 80° .

The specific gravity of iodine trichloride cannot be determined by any of the customary methods, on account of the facility with which this compound volatilises and decomposes; in fact it maintains a constant weight only at comparatively low temperatures in an atmosphere of chlorine or carbon dioxide. The following method of determining the specific gravity, which may be applicable also in the case of other easily decomposable bodies, is described by Christomanos (*Berl. Ber.* x. 782; *Chem. Soc. J.* xxxii. 697). A thin-walled glass vessel furnished with two glass taps, and holding about a litre, is filled with chlorine and weighed, the chlorine then expelled by carbon dioxide, and the vessel again weighed. The iodine trichloride is next introduced into the vessel, chlorine passed through, and another weighing made. The resulting increase of weight is equal to the weight of the iodine trichloride less that of the chlorine which it displaces. The chlorine is then displaced by carbon dioxide, and the vessel is again weighed, whereby the weight of the trichloride is obtained less that of an equal volume of carbon dioxide which it displaces; and as the weights of the equal volumes of chlorine and carbon dioxide thus displaced stand to one another in a known proportion, the weight of a volume of chlorine equal to that of the iodine trichloride, and the weight of the trichloride itself, can be determined by calculation. Hence also the weight of the trichloride compared with that of an equal bulk of water, that is to say, its specific gravity, can be found. The number found by Christomanos was 3.1107; but as the experiments were made with a very imperfect apparatus, this number is regarded as only approximate.

Oxides and Oxygen-acids of Iodine. *Iodine Trioxide* or *Iodous Oxide*, I_2O_3 , is formed, together with the pentoxide, which is the ultimate product, by the action of ozone on iodine. It is a light-yellow, extremely light powder, which deliquesces to a syrup in moist air, and is resolved, on addition of more water, into free iodine and iodic acid. Heated to 125° – 130° , it decomposes violently, with evolution of iodine and free oxygen, leaving a small white residue of iodic oxide, which is decomposed at a higher temperature into iodine and oxygen (J. Ogier, *Compt. rend.* lxxv. 957).

Iodic acid, IO_3H . *Reactions, Detection, and Estimation.*—Iodates in solution are reduced to iodides by the action of the copper-zinc couple (Thorpe, *Chem. Soc. J.* 1873, 541).

According to Jacquemin (*Compt. rend.* lxxvii. 211), small quantities of iodic acid or its salts may be readily detected by means of *pyrogallol*, which instantly turns them brown and produces a precipitate of purpuro-gallin (1st *Suppl.* 977). As pyrogallol does not act in a similar manner on the acids of chlorine and bromine, or on nitric acid, this test may be used for the detection of iodic acid in nitric acid, and of iodates in potassium iodide solution, urine, and other liquids.

Action of Phosphorus.—Sonstadt (*Chem. News*, xxviii. 288) employs for the detection of small quantities of iodates—in sea-water for example—carbon disulphide containing in solution a small quantity of phosphorus. An excess of phosphorus must be avoided, as it would destroy the coloration by converting the reduced iodine into hydriodic acid. According to Corne (*J. Pharm.* [4], xxii. 425), the separation of iodine from iodates in solution may also be effected by addition of a few drops of water in which phosphorus has been kept, the effect being due to the presence of phosphorous acid in the liquid, inasmuch as it is not produced by a piece of clean phosphorus. Polacci, on the other hand (*Gazz. chim. ital.* 1873, 474) ascribes the reduction to the direct action of the phosphorus; he finds, moreover, that it is produced by amorphous phosphorus. If the liquid is alkaline, it must first be neutralised. Corne (*J. Pharm. Chim.* [4], xxiv. 216), from further experiments maintains the correctness of his former view.

Iodic and Periodic acid may be separated by the different behaviour of their barium-salts to ammonium carbonate, the iodate being easily converted by digestion with ammonium carbonate, even at ordinary temperatures, into barium carbonate and ammonium iodate, whereas the periodate when similarly treated remains unaltered (Kämmerer, *Zeitschr. anal. Chem.* 1873, 377).

Constitution and Basicity of Periodic Acid.—Thomsen, from his experiments on the heat of neutralisation of periodic acid, inferred that, of the five hydrogen-atoms in the ordinarily assumed molecule of this acid, H_5IO_6 , two only are normally basic; in other words that the acid must be regarded as pentahydric (or pentatonic) and bibasic (2nd *Suppl.* 681). The same view is taken by Basarow (*Berl. Ber.* vi. 92), who represents periodic acid by the formula $(\text{HO})_2\text{IO}$, in which the iodine is septivalent, two of the five hydroxyl-groups being acid, the other three alcoholic.

Sodium Periodate.—A crystalline periodate of sodium is precipitated when an iodide or iodate is heated with a hypochlorite and excess of alkaline hydrate, in presence of sodium salts. As this precipitation takes place only when sodium salts are present, it may be used as a test for sodium (T. Fairley, *Rep. Br. Assoc.* 1875, [2], 42).

iodoform, CHI_3 . This compound is produced, together with acetic acid, by the action of iodine and ammonia on monobromacetone (Sokolowsky, *Berl. Ber.* ix. 1687).

To prepare iodoform, R. Rother (*Pharm. J. Trans.* [3], iv. 593) heats 32 pts. iodine, 32 potassium carbonate, 16 alcohol of 95 per cent. and 80 water, till the mixture becomes colourless; then decants the clear liquid; collects the separated crystals of iodoform; and mixes the filtered liquid with 16 to 24 pts. hydrochloric acid and 2 to 3 pts. potassium dichromate. The liquid is then neutralised with potassium carbonate, and 32 pts. more of that salt are added, together with 6 pts. iodine and 16 alcohol. The reaction having been completed at the heat of the water-bath, the product is treated as above, whereby a fresh quantity of iodoform is obtained. The object of the treatment with potassium chromate and hydrochloric acid is to set free the iodine present as potassium iodide by the action of the chlorine thereby evolved, and thus render it available for the reaction.

On the Crystalline Form of Iodoform, see Dogiel (*N. Petersb. Acad. Bull.* xx. 337).

IRIDIUM. On alloys of Iridium and Platinum, and on the Separation of these two Metals, see PLATINUM.

IRIS ROOT. The crystalline odoriferous principle obtained by distilling this root with water has been examined by Flückiger (*Arch. Pharm.* [3], viii. 481), who

finds that it consists of crystals of myristic acid saturated with a fragrant oil. The myristic acid does not appear to be present in the root in the free state, but to be separated by the process of distillation from a compound existing therein.

IRON. *Occurrence.*—The metallic iron found by Nordenskiöld near Disco Bay, in Greenland (2nd Suppl. 796), and supposed to be of meteoric origin, has been examined by Steenstrup, who infers, from its mode of occurrence and its structure, that it is of terrestrial origin, an opinion in which Rammelsberg concurs (*Zeitschr. geol. Ges.* xxviii. 225; *Jahrb. f. Min.* 1877, 91; *Chem. Soc. J.* xxxii. 578).

On Meteoric Iron, see METEORITES.

On the occurrence of Iron ores in various countries, and the minerals accompanying them, see *Jahresb. f. Chem.* 1875, 1265.

Physical Properties.—On the influence of Heat, and of the passage of an Electric Current, on the Electric Conductivity of iron and steel, see ELECTRICITY (p. 718). On the Heat-conductivity of iron, see HEAT (p. 1017).

Influence of Magnetisation in the Molecular Structure of Iron.—Faraday showed that iron loses its magnetism at a high temperature, and recovers it at a certain point as the temperature falls. W. F. Barret (*Phil. Mag.* [4], xlvii. 51) finds that at this particular temperature an iron wire experiences an alteration of structure attended with sudden elongation, and a change of place of the metal in the thermo-electric scale; at the same time it emits a sound, and glows more brightly for a short time, just before its incandescence ceases altogether. The thermic and electric conducting powers of the wire appear to be altered at the same time. Barret also observes that a very hard and tough iron can be produced by the action of a strong electromagnet on the metal while in a state of fusion.

Occlusion of Gases by Iron.—Iron precipitated by the voltaic current from a solution of neutral ferrous chloride and sal-ammoniac (shining brittle nodules which scratch glass) gives off hydrogen when immersed in water or other liquid. By exposure to the air it loses only a portion of the absorbed gas. In hot water the evolution of gas from the iron is very rapid, and is sometimes attended with an audible sound. The occluded gas is given off when the iron is heated in a vacuum. One vol. iron thus treated gave off 235.8 to 248 vol. hydrogen. The iron, after it has been heated, takes up no more hydrogen, even when it is employed as the negative electrode of a voltameter. The hydrogenised iron is very hard and possesses considerable coercitive power (Cailletet, *Compt. rend.* lxxx. 319).

According to O. Reynolds (*Institut.* lxxiv. 270), iron takes up hydrogen when acted upon by dilute sulphuric acid. Iron or steel thus treated becomes shortened and brittle, increases in weight, and gives off hydrogen when immersed in water.

On the Occlusion of Gases by Cast Iron and Steel, see IRON METALLURGY (p. 1112).

Influence of various Solutions on the Rusting of Iron.—A. Wagner has examined the action produced on strips of iron by water containing various salts, in presence of air free from carbon dioxide, and of air containing that gas, at various temperatures; also in sealed tubes from which air was expelled.

The experiments show that pure water in presence of air causes iron to rust; that if carbon dioxide is also present, the rusting is more rapid; that the production of rust is materially increased by the chlorides of magnesium, ammonium, sodium, potassium, barium, and calcium, the first mentioned being the most active in this respect; that iron immersed in evaporated river-water rusts more slowly than iron in distilled water; that the presence of oils or fats greatly diminishes the rapidity of rusting; and that alkalis prevent the rusting entirely. Magnesium chloride solution in the absence of air attacked iron at a temperature of about 100°; the chlorides of sodium, potassium, barium, and calcium were without action under the same circumstances.

Compounds of Iron.

Alloys. An alloy of iron and Chromium containing 74 per cent. Cr, 25 per cent. Fe, and 1 per cent. foreign matter, has been obtained by reducing chrome-iron ore (from the Ural) with charcoal; it has a silvery fracture, and the hardness of diamonds. In some trials alloys capable of welding were formed; they contained 98.4 per cent. iron, 2.3 chromium, 1.3 lime and silica, and traces of carbon (S. Kern, *Chem. News*, xxii. 136, 265).

An easily fusible alloy, which filled the moulds well, was found to contain 79 per cent pig-iron, 19.5 tin, and 1.5 lead (Kern, *loc. cit.*)

On alloys of Iron and Manganese, see IRON METALLURGY (pp. 1108–1111). On alloys of Iron and Copper, see COPPER (p. 566).

Amalgamation.—An amalgam of iron is easily obtained by bringing cleansed iron in contact with sodium- or ammonium-amalgam, and when it has become covered with

a silvery coating, dipping it into acidulated water; the sodium- or ammonium-amalgam is then decomposed, and the mercury penetrates the iron. An iron plate is also quickly amalgamated when made to serve as the negative electrode of a battery with mercury and acidulated water. The best results are, however, obtained by the use of zinc-amalgam. The mercury is covered with dilute sulphuric or hydrochloric acid, and the iron is placed in the liquid, together with some pieces of zinc, whereupon it quickly becomes covered with mercury. The quantity of mercury thus precipitated on the iron is very small; nevertheless, it does not merely form a superficial deposit, but penetrates deep into the iron, modifying its chemical and physical properties. Amalgamated iron, like amalgamated zinc, is less easily attacked by acids than the metal in its ordinary state.

Cyanides. See pp. 611-616.

Nitride, $\text{Fe}^{\text{III}}\text{N}_2$. This compound has been found by Silvestri (*Pogg. Ann.* clvii. 165) in silvery-lustrous deposits on the lavas of Etna. It may be formed artificially by heating the lava first in a stream of hydrogen chloride, to decompose it, and then in a stream of dry ammonia gas; also, though less easily, by the action of sal-ammoniac vapours on the ignited lava. On fusing it with sulphur, sulphide of iron is formed and nitrogen is evolved.

Frémy (*Compt. rend.* lii. 321) assigns to the artificial compound the formula $\text{Fe}^{\text{III}}\text{N}_2$; by Stahlschmid (*Pogg. Ann.* cxv. 321) it is regarded as $\text{Fe}^{\text{IV}}\text{N}_2$, and by Rogstadius (*J. pr. Chem.* lxxxvi. 307) as $\text{Fe}^{\text{VI}}\text{N}_2$. The natural product heated in a stream of hydrogen yields metallic iron and ammonia, in quantities which show that the composition of the nitride is 90.86 per cent. iron, and 9.14 nitrogen, agreeing with Frémy's formula.

Silvestri considers it very probable that this iron nitride, for which he proposes the name 'Siderazote,' has played a very important part in volcanic processes, as it appears that the metallic-shining compound is peculiar to blocks of lava possessing sharp edges, found in the neighbourhood of craters, and in the middle of lava streams. Lava may possess the property of absorbing nitrogen under certain conditions of temperature, and thus give rise to the formation of ammonium chloride, which is found so largely as a product of the fumaroles in crevices and holes. The decomposition of this ammonium chloride in presence of ferruginous lava may explain the presence of hydrogen amongst the products of volcanic action.

Oxides. Ferric oxide prepared from the oxalate, when heated for half an hour to 350° in a current of hydrogen, furnishes the magnetic oxide; if it be heated for twenty minutes to 500° , ferrous oxide is produced in the pyrophoric state. Ferrous oxide thus prepared decomposes water, slowly at ordinary temperatures, more rapidly at 100° . In contact with nitric acid, it exhibits vivid incandescence. With carbon dioxide at 500° it forms carbon monoxide and magnetic oxide of iron: $3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$, a reaction which explains why ferrous oxide cannot be obtained by heating the carbonate, unless the heat be very gentle. Pyrophoric ferrous oxide displaces a part of the ammonia in ammonium sulphate, forming ammonio-ferrous sulphate. Carbon dioxide has no effect on it at the ordinary temperatures, nor does exposure to a temperature of 450° in an atmosphere of nitrogen deprive it of its pyrophoric properties.

If ferric oxide be reduced by hydrogen at 700° , non-pyrophoric metallic iron is produced. Carbon monoxide produces the same effect as hydrogen, forming magnetic oxide at 350° , pyrophoric ferrous oxide at 500° , and metallic iron at 700° to 800° .

The same results are obtained when the reductions are effected at the same temperature, but for different lengths of time; thus, at 440° , ferrous oxide is obtained after six hours, and metallic iron after twelve hours' reduction; at 350° magnetic oxide is obtained after one hour, ferrous oxide after ten hours, and metallic iron after thirty-six hours (H. Moisson, *Compt. rend.* lxxiv. 1296).

Ferric Oxide, Fe_2O_3 .—A. Frenzel (*Jahrb. f. Min.* 1874, 685) accidentally obtained small rhombohedrons of iron-glance, slightly magnetic and having a metallic lustre, by igniting a precipitate of ferric hydrate.

Ferric Oxide from Meteoric Iron.—Ignited ferric oxide prepared from meteoric iron is attracted by the magnet, whereas the oxide prepared from ordinary iron does not exhibit this property after ignition; when dried at 110° it is slightly attracted, but this property is feeble the higher the temperature at which the oxide has been dried. With the sesquioxide prepared from meteoric iron the case is exactly the reverse. The magnetic properties of the oxide thus prepared are due to the presence of small quantities of nickel or cobalt-salts; and when these have been removed by four successive precipitations and redissolutions in sodium acetate, the ferric oxide exhibits all the properties of that which is obtained from terrestrial sources. On the other hand by adding small quantities of cobalt or nickel (or both) to a ferric salt,

and precipitating with ammonia, an oxide is obtained having all the properties of that which is prepared from meteoric iron. It is possible that the presence of the nickel or cobalt may give rise to the formation of $\text{Fe}^{\text{Ni}}\text{O}^4$, or that, as suggested by C. F. Chandler, the oxide of cobalt or nickel may unite with the ferric oxide to form the compounds, $\text{Fe}^{\text{Co}}\text{O}^4$ and $\text{Fe}^{\text{Ni}}\text{O}^4$, analogous to $\text{Fe}^{\text{Ni}}\text{O}^4$ (J. L. Smith, *Amer. Chemist*, v. 356).

Reduction of Ferric Oxide by Carbon.—J. Parry (*Chem. News*, xxvii. 313) found that when pure ferric oxide was heated in a vacuum with pure carbon, obtained by calcination of white sugar, no gas was evolved at 100° , but that between the melting points of lead and copper 77 per cent. of the oxygen in the ferric oxide was removed in seventeen hours, slowly at the lower temperatures, with formation chiefly of carbon dioxide, rapidly at the higher temperatures, the gas then evolved consisting chiefly of carbon monoxide. These facts seem to show that solid carbon may play some part in the chemistry of the blast-furnace.

Reduction by a mixture of Carbon Dioxide and Cyanogen.—This mixture at high temperatures exerts a strong reducing action, stronger indeed than that of a mixture of CO^2 and CO. With 1 vol. CN and 6 vol. CO^2 at 685° – 710° F., the ferric oxide is deprived of 79.9 per cent. of its oxygen, yielding 56.3 per cent. metallic iron. If the proportion of CO^2 be increased to 15 vol., only 6.5 per cent. of metallic iron is obtained, and with 30 vol. CO^2 , the yield of iron is reduced to 0.9 per cent. Part of the carbon formed unites with the reduced iron.

Ferric Hydrate. *Limonite*, $\text{Fe}^{\text{H}}\text{O}^3$ or $2\text{Fe}^{\text{H}}\text{O}^3 \cdot 3\text{H}^2\text{O}$, occurs at Big Lick, Roanoke County, Virginia, in narrow veins having the lustre and translucency of goëthite. These veins, which traverse the ordinary compact limonite, are dark blood-red by transmitted, nearly black by reflected light. Lustre between adamantine and waxy. Streak yellowish brown. Hardness somewhat above 5. Sp. gr. 3.76 at 15° .

Composition.—A. Direct result of analysis. B. After deduction of phosphoric acid and of 2.68 per cent. $\text{Fe}^{\text{H}}\text{O}^3$ as FePO^4 , also of the water given off at 100° . C. Values calculated from the formula $\text{Fe}^{\text{H}}\text{O}^3$:

	$\text{Fe}^{\text{H}}\text{O}^3$	$\text{Mn}^{\text{H}}\text{O}^3$	$\text{Al}^{\text{H}}\text{O}^3$	$\text{P}^{\text{H}}\text{O}^3$	SiO^2	H^2O	
A (found)	81.52	0.11	0.26	2.38	0.51	14.95	= 99.73
B (corr.)	85.61	—	—	—	—	14.39	= 100
C (calc.)	85.56	—	—	—	—	14.44	= 100

Of the 14.95 per cent. H^2O , 1.70 goes off at 100° , 0.93 at 150° , 3.60 at 200° , 5.01 at 250° , and 3.74 at a red heat (Mallet, *Sill. Am. J.* [3], ix. 460).

Compound of Ferric Oxide with Lime, $\text{Fe}^{\text{H}}\text{O}^3 \cdot \text{CaO}$ or $(\text{FeO}^2)^2\text{Ca}$.—This body is formed when a mixture of 190 pts. iron and 66.5 lime is heated to whiteness for several hours in a platinum crucible standing in a muffle, and the mixture is left to cool slowly. It is thus obtained in crystals often an inch long, and having a strong metallic lustre. Still larger crystals of the same compound are obtained by igniting 1000 grains of hematite with 1000 grains of chalk. It is magnetic, has a sp. gr. of 4.693, and yields a red-brown powder (J. Percy, *Phil. Mag.* [4], xlv. 455).

Ferroso-ferric Oxide, Magnetic Oxide, $\text{Fe}^{\text{H}}\text{O}^3$.—A mixture of this oxide with corundum, forming a thick bed at Sheep's Hill near Cruger on the Hudson, is described by J. Kamball (*Amer. Chem.* iv. 321; *Jahresh. f. Chem.* 1874, 1078). Being a very basic and therefore very refractory mineral and rich in ferric oxide, it is well adapted for the fettling of puddling furnaces, and as an oxidising material in the Bessemer converter.

Ferroso-ferric Oxide from Aniline residues.—The residue left in the preparation of aniline by the action of ferrous acetate on nitrobenzene consists of magnetic iron oxide, $\text{Fe}^{\text{H}}\text{O}^4$, agreeing in composition with the native oxide from Cornwall and Dannemora, as shown by the following analysis:

$\text{Fe}^{\text{H}}\text{O}^3$	FeO	Graphite	SiO^2	$\text{P}^{\text{H}}\text{O}^3$	S and Mn	
67.00	30.05	1.23	0.78	0.62	traces	= 99.68

(J. Spiller, *Berl. Ber.* vi. 1384).

Oxysalts of Iron. See the several acids.

Phosphide. On triferrous phosphide, $\text{Fe}^{\text{P}}\text{P}^2$, produced by the action of phosphine on a solution of a ferrous salt, see 2nd Suppl. 949.

Sulphides. The *Monosulphide*, FeS, may be prepared by heating a mixture of 2 pts. iron pyrites and 1 pt. iron-filings to redness for half-an-hour in a hessian crucible (C. Méhu, *Russ. Zeitschr. Pharm.* 1876, 546).

The *Sesquisulphide* or *Ferric Sulphide* is precipitated as a hydrate, $2\text{Fe}^{\text{S}}\text{P}^2 \cdot 3\text{H}^2\text{O}$, by the action of yellow ammonium sulphide on a solution of ferric chloride containing free chlorine or a small quantity of sodium hypochlorite. As thus

obtained, it is a green flocculent precipitate, becoming almost black after washing on the filter. On mixing it, after drying, with a white powder, such as chalk, the green colour is again distinctly seen. The sesquisulphide is soluble in ammoniacal water, and is precipitated therefrom on dilution: it dissolves also in alcoholic ammonia, forming a perfectly clear, emerald-green solution which can be filtered. In a mixture of ammonium sulphide and very dilute ammonium thiosulphate, it is but slightly soluble. It dissolves in hydrochloric acid, with evolution of hydrogen sulphide and formation of ferric chloride (Phipson, *Chem. News*, xxx. 139).

Bisulphide, FeS_2 . Iron pyrites.—Observations on the formation of pyrites in recent times have been made by Daubrée (*Compt. rend.* lxxxi. 854; *Chem. Soc. Jour.* xxix. 533). He points out that, frequent as the formation of iron sulphide may be, it is but rarely that the product is a true pyrites, that is to say, a crystalline, metallically lustrous sulphide, capable of resisting the action of acids. Amongst localities in which true pyrites has been formed in historic times, may be especially mentioned the warm springs of Bourlonne-les-Bains (Dép. Haute Marne) and of Hamman-Meskoutin in the province of Constantine, Algeria. At the former locality, pyrites is found in small granules mixed with the sand near the source of the spring, and as a coating on quartz-grains and remains of flint implements, whereby its recent origin is sufficiently indicated, also in small cavities in the lime between the tiles of an old conduit, which likewise contains crystals of calc spar. The reaction in this case appears to be similar to that observed by Ebelmen between calcium sulphate and ferric oxide, in presence of organic matter, whereby iron bisulphide and calcium carbonate were produced. Daubrée also mentions the occurrence of pyrites in a fissure of a ship's timber which, before being used for building, had lain for some time in a basin receiving the contents of two sewers, whereby reducing and sulphuretted compounds were probably introduced into the water.

Detection and Estimation of Iron, and Analysis of its Compounds.

The smallest trace of iron in a nickel-salt may be easily detected by mixing the slightly acidulated solution with *potassium thiocyanate*, and agitating with ether. A rose tint in the ethereal layer indicates with certainty the presence of iron (Böttger, *N. Rep. Pharm.* xxiv. 621).

Estimation of Ferric Oxide and Alumina in presence of Phosphoric Acid.—To the liquid containing phosphoric acid, alumina, and oxide of iron, an excess of calcium chloride is added, and then ammonia, which throws down tricalcic phosphate, alumina, and ferric oxide. The precipitate is ignited, weighed, and dissolved in hydrochloric acid; the phosphoric acid is determined by means of uranium in one portion of the solution, and the iron by stannous chloride in another. The phosphoric acid is calculated into tricalcic phosphate, and the iron into Fe_2O_3 , and the difference between the united weights of these compounds and that of the original precipitate gives the alumina. If sulphuric acid is present, it must be separated by baryta before the addition of ammonia. The presence of baryta in the filtrate does not affect the results, provided sufficient calcium chloride is added to precipitate all the phosphoric acid, as $\text{P} \cdot \text{O}^5(\text{CaO})^3$ (H. Pellet, *Bull. Soc. Chim.* [2], xxvii. 106).

Volumetric Estimation. 1. With *Sodium Thiosulphate* (iii. 385).—To render this method exact, it is desirable that the iron solution should be as nearly neutral as possible, since an excess of acid would decompose the thiosulphate. J. M. Crafts (*Bull. Soc. Chim.* [2], xx. 50) employs for the titration: (1). A $\frac{1}{20}$ -normal solution of thiosulphate prepared by dissolving 12.4 grams of the air dried salt in a litre of water. 2. A $\frac{1}{20}$ -normal solution of ferric chloride, which serves for the exact titration of the thiosulphate solution, and is best prepared by dissolving the required quantity of iron containing a known amount of carbon in hydrochloric acid, with addition of a little nitric acid, and evaporating down till a drop taken out just dissolves in water without turbidity.

For the estimation of iron in ores, the pulverised ore is digested with strong hydrochloric acid, with addition of a little nitric acid, to convert the whole into ferric salt, and the solution is freed from excess of acid by neutralisation with sodium carbonate, or better by cautious evaporation. It is advisable to use 1.4 grm. of the ore and dilute the solution to half a litre. The number of c.c. of thiosulphate solution required for the decomposition of 100 c.c. of the iron solution, will then give the percentage of metallic iron in the ore. The first titration serves for the approximate estimation of the quantity of thiosulphate required; in the subsequent operations, about 20 per cent. more of the thiosulphate is taken, and the excess determined by back-titration in the usual way with iodine and starch. The operation is somewhat impeded by the presence of considerable quantities of sulphates, phosphates, and in general of any acids which readily form precipitates with the iron. The presence of atmospheric oxygen in the water used does not create any difficulty.

2. With *Permanganate*.—Parnell (*Chem. Soc. Jour.* xxvi. 27) recommends that the estimation of iron by permanganate be performed by candle or gas light, so that the disturbing influence caused by the yellow colour of the resulting ferric salt on the exact recognition of the end of the operation may as far as possible be eliminated. A solution of 3 pts. ferric chloride in 400 pts. of water is colourless by candle-light, but the slightest trace of permanganate added to it produces a perceptible coloration. For the titration of the permanganate solution, Parnell recommends *arsenious acid*, as it can easily be obtained quite pure, and the inconvenience arising from the slowness of the action towards the end of the oxidation, and from the brown coloration of the liquid resulting from the formation of manganic oxide, may be obviated by addition of a slight excess of a standard solution of a ferrous salt, the excess of ferrous oxide in which can be very exactly determined by back-titration with permanganate solution.

A simple method of estimating iron in ores, *without the use of weights*, is described by W. N. Hartley (*Chem. Soc. Jour.* xxviii. 410). A suitable quantity of the ore is counterpoised by pure iron wire; the ore and wire are dissolved in separate quantities of acid; the two solutions are made up to equal volumes; and $\frac{1}{50}$ of the total volume of each is taken for the analysis, whereby the error in weighing is reduced to $\frac{1}{50}$. The two ferric solutions are then reduced by granulated zinc, and titrated with permanganate. If then m and n denote the quantities of permanganate solution used for the solution of the ore and of the wire respectively, the percentage x of iron in the ore is given by the equation:

$$x = \frac{m}{n} \cdot 100.$$

3. With *Potassium Dichromate*.—The titration of ferrous salts with a standard solution of potassium dichromate is regarded by Riley (*Chem. Soc. Jour.* xxxii. 25) as the best of all methods for the volumetric estimation of iron. W. I. Howie (*Pharm. J. Trans.* [3], vi. 480) points out that it is apt to give too high a result, if sugar is present, and the titration is performed in a hydrochloric acid solution. In such cases, as in the analysis of *Ferrum carbonicum saccharatum*, he recommends that the iron salt be dissolved, not in hydrochloric, but in phosphoric acid, since, in presence of this acid, the dichromate is not reduced by sugar.

4. With *Stannous Chloride*.—To the method of estimating iron by means of standard solutions of stannous chloride, recommended by Fresenius and others (iii. 385), two objections have been raised, viz.: First, that the solution of stannous chloride rapidly decomposes, and has constantly to be re-standardised; secondly, that the results are not constant, the same weight of ore requiring varying amounts of standard solution. The first objection is met by keeping the standard solution in a bottle to which the air can have access only through a wash-bottle of potassium pyrogallate. When the solution is kept in this manner, the variation in four weeks is under 0.1 p.c. The second objection is untenable, since, when the solution is strongly acid and hot, the limits of error can be confined to 0.05 p.c. The extreme sharpness, and above all the rapidity of the operation, render it very advantageous, especially in mining practice (Uelsmann, *Zeitschr. anal. Chem.* xvi. 50). See also Stock and Jack (*Chem. News*, xxx. 221; xxxi. 63); Esilmann (*ibid.* 221); C. W. Hinman (*Sill. Am. J.* [3], xiv. 478; *Chem. Soc. Jour.* xxxiv. 608).

Carnelley (*Chem. News*, xxx. 257) estimates iron in well-water colorimetrically by adding to a measured volume of the water, after oxidation of the iron by permanganate solution and sulphuric acid, a known quantity of solution of *potassium ferrocyanide*, and comparing the tint of the resulting blue liquid with that of another, prepared by adding a titrated iron solution to the same quantity of potassium ferrocyanide dissolved in a correspondingly large volume of distilled water.

Separation of Iron from Uranium. According to E. Burcker (*J. Pharm. Chim.* [4], xxvii. 347), the method of separating these metals based on the precipitation of the iron with ammonium carbonate (v. 944) is not very exact, as, after a short time, the double carbonate of uranium and ammonium is likewise deposited, and is very difficult to remove from the precipitate. Better results are obtained by the following method given in Rose's *Traité d'Analyse Quantitative*. The solution of ferric and uranic salt is precipitated by ammonia; the precipitate, after ignition and weighing, is heated in a current of hydrogen, and the reduced iron is dissolved out by dilute hydrochloric acid, brought to the state of ferric salt by nitric acid, and precipitated by ammonia.

On the separation of Iron from *Uranium* and *Chromium*, see p. 458.

Analysis of Cast Iron and Steel.

An elaborate memoir on the estimation of the several constituents of iron and steel has been published by M. Boussingault (*Ann. Chim. Phys.* [5], v. 148). 1. To estimate the carbon, the finely-pulverised metal is triturated with 16 to 20 times its weight of mercuric chloride, and the insoluble mixture of carbon and mercurous chloride which remains after boiling the whole with hydrochloric acid, then washing and drying, is placed in a platinum boat, and heated to dull redness in a stream of hydrogen in order to drive off the mercurous chloride. The residue of carbon-compounds and graphite remaining in the boat is then weighed and heated, first over a lamp to burn away the carbon-compounds, afterwards in a stream of oxygen to burn the graphite. The accuracy of the determination may be increased by receiving the carbon dioxide produced by the combustion in a weighed absorption apparatus, as in organic analysis. This method, besides showing the form in which the carbon is present in the iron, has the further advantage of rendering visible extremely small quantities of carbon, even a small fraction of a milligram being easily recognised on the bottom of the platinum boat. The accuracy of the result is not impaired by the presence of nickel, copper, or chromium, since these metals, like the iron, are converted into chlorides, and pass into solution. The presence of tungsten, however, creates a difficulty, as this metal remains behind together with the carbon and the mercurous chloride, and is converted into oxide during the combustion of the carbon, thereby compensating wholly or partially the loss of weight. Moreover the tungstic acid formed at a red heat may burn a portion of the graphite to carbon dioxide. Hence, when the proportion of tungsten is considerable, it is best to estimate the carbon by direct combustion and weighing of the carbon dioxide.

Silicon.—To obtain an exact estimation of this element, especially when its amount is very small, the analysis must be made in the dry way, inasmuch as liquid reagents almost always contain traces of silicon, which may also be imparted from the glass or porcelain vessels in the process: If, on the other hand, the comminuted iron be first oxidised on the platinum boat in a muffle furnace, and then ignited in a stream of dry hydrogen chloride, pure silica will be left in the boat.

Phosphorus is estimated by dissolving the iron in nitric acid, evaporating, and calcining the residue, fusing the resulting oxide with sodium carbonate, boiling the melt with water, acidulating with nitric acid, and precipitating with an ammonio-ceric salt. The precipitate of cerium phosphate is then decomposed by oxalic acid, and the phosphoric acid in the filtrate is determined as ammonium-magnesium phosphate. The phosphoric acid may also be precipitated from the nitric acid solution by ammonium molybdate.

Sulphur is determined by passing the gas evolved on treating the iron with dilute sulphuric acid into a solution of silver nitrate, whereby the whole of the sulphur is precipitated as silver sulphide.

Manganese.—For the estimation of this metal, Boussingault finds that the iron (as ferrie salt) may be completely precipitated by sodium acetate. When the quantity of manganese is very small, the nitric acid solution may also be treated with lead dioxide, and the resulting red solution titrated back with mercurous nitrate, the strength of which has been determined by means of an iron solution containing a known amount of manganese.

The precipitation of manganese as peroxide by the electric current is not to be recommended, on account of the time which it takes, and the various disturbing influences which affect the result.

For the estimation of the iron itself, Boussingault gives the preference to the method with permanganate; and for the detection of copper he recommends the known process founded on the separation of copper and iron by ammonia, and the extremely delicate reaction with ferrocyanide.

On the analysis of Carburetted Iron see also C. H. Piesse (*Chem. News.* xxix. 57 and 110; *Chem. Soc. J.* xxvii. 711); A. H. Allen, *Chem. News.* xxix. 91 and 120); H. Uelsmann, *Dingl. pol. J.* cxxx. 534; *Jahresb. f. Chem.* 1876, 999).

The following methods relate to the determination of special constituents:

J. Parry (*Amer. Chemist*, iv. 257) estimates the carbon in pig iron by dissolving the metal in solution of cupric sulphate, burning the dried residue of copper and carbon with cupric oxide, and instead of absorbing the carbon dioxide in a potash apparatus, passing it, by means of a Sprengel pump, into a graduated cylinder, and measuring it, with the necessary corrections for pressure, temperature, and moisture.

Uelsmann (*Dingl. Pol. J.* cxxx. 534), after dissolving the iron in a solution of cupric chloride, oxidises the carbon with chromic acid, as recommended by Ullgren

(*Liebig's Annalen*, cxxiv. 59), in an apparatus connected with a cooled receiver, the operation being assisted by heat, and the evolved carbon dioxide absorbed by soda-lime.

For the estimation of carbon in spiegeleisen, Riley (*Chem. Soc. J.* xxxii. 1) dissolves the metal in cupric chloride, and, after complete solution of the iron and of the precipitated copper, collects the carbon, &c., on an asbestos filter, and burns the carbon with cupric oxide in a current of oxygen. For high percentages of carbon Riley considers that colorimetric determinations are not satisfactory.

For the estimation of phosphorus, Uelsmann (*Dingl. pol. J.* cxxviii. 492) regards the method of precipitation with molybdic acid as the only one capable of affording exact results in the analysis of pig iron, steel, &c. The best way of proceeding, as proposed by Eggertz (*J. pr. Chem.* lxxix. 496), is to weigh the precipitate directly, as when dried at 110° – 120° it always contains the same quantity of phosphorus (1.63 per cent.), provided the process be carried out under uniform conditions. It is especially important that no acid, except nitric acid, be present, and that the precipitate be quickly formed.

Koschelt (*Chem. Centr.* 1877, 487) prepares a molybdic solution by dissolving 1 part of pure molybdic acid together with 1 part of caustic potash in 6 parts of water; adding, after cooling, a solution of $\frac{1}{2}$ part of tartaric acid in 2 parts of water, followed by addition of $7\frac{1}{2}$ parts of nitric acid; heating the whole to boiling; and filtering while hot. About 1 gram of the iron is dissolved in the smallest possible quantity of nitric acid (the solution should not measure more than 50 c.c.), and the filtered liquid is allowed to flow into about 30 c.c. of the molybdic solution placed in a basin on the water-bath. After complete precipitation, the whole is warmed for a short time; and the precipitate is collected on a weighed filter, washed with dilute nitric acid (2 : 3) and alcohol, dried at 120° – 130° , and weighed: it contains 1.73 per cent. of phosphorus. Cairns (*ibid.*) precipitates the ferric phosphate with ammonia, redissolves, precipitates with ammonium molybdate, redissolves, reprecipitates, again dissolves, and finally precipitates with magnesia mixture.

A spectroscopic method of estimating phosphorus in iron and steel is given by J. Alleyne (*Institut*, 1875, 253), depending on the fact that when an electric spark is made to pass between iron electrodes, the presence of phosphorus may be recognised by certain characteristic lines, which disappear completely when the atmospheric air surrounding the electrodes is replaced by an atmosphere of hydrogen, and reappear when oxygen is again admitted into the tube, the quantity of oxygen required to reproduce them being inversely proportional to the amount of phosphorus in the iron.

Sulphur may be estimated by dissolving the iron in dilute sulphuric acid, and passing the gas, which contains hydrogen sulphide if sulphur is present, into an alkaline solution of lead oxide, whereby the sulphur is precipitated as lead sulphide, which may then be oxidised to sulphate. The operation should be conducted in an atmosphere of hydrogen, since, if air is passed for a long time through the alkaline lead solution, the precipitated lead sulphide becomes oxidised and dissolves in the alkaline liquid (Fresenius, *Zeitschr. anal. Chem.* 1874, 39). J. Moffat Johnson (*ibid.*) uses, instead of the alkaline lead solution, a solution of bromine in hydrochloric acid, whereby the hydrogen sulphide is immediately converted into sulphuric acid. Th. M. Drown (*Amer. Chemist*, iv. 423) effects the oxidation of the hydrogen sulphide by passing it through at least three bottles containing solution of potassium permanganate (1 : 200).

Aluminium and Chromium. For the determination of these metals the following method is given by A. Blair (*Sill. Am. J.* [3], xiii. 421). Five grams of iron or steel borings are placed in a half-litre flask with 20 c.c. of hydrochloric acid diluted with three or four times its volume of water, and the flask is closed with a valved stopper. If necessary, heat is applied, and when the iron is dissolved, the valved stopper is replaced by a solid one, and the flask cooled. The flask is then about three-fourths filled with water and a slight excess of barium carbonate (free from sulphate) added gradually. The flask should be thoroughly shaken several times, loosening the stopper occasionally to allow the carbonic acid to escape, and left over-night. The liquid is then quickly filtered, and the precipitate washed with cold water and dissolved in hydrochloric acid; the solution diluted; the sesquioxides of iron and chromium precipitated with ammonia; and the excess of ammonia expelled by boiling. The precipitate is washed, dried, and fused with 3 grams of sodium carbonate and 0.5 gram of nitre, the heat being continued till all the nitre is decomposed; the fused mass is dissolved in water; and the solution filtered from the ferric oxide, is evaporated with hydrochloric acid and alcohol. The chromic oxide which remains is then dissolved in hydrochloric acid, the solution filtered from silica, and the chromium precipitated in the usual way.

For the determination of aluminium in steel, the first part of the process is the same as for chromium, as far as the washing of the precipitate obtained with barium carbonate, which in this case is dissolved in hydrochloric acid and the barium precipitated with sulphuric acid; the barium sulphate is then removed and the excess of acid expelled by evaporation. The ferric oxide, alumina, and chromic oxide, are separated by ammonia, ammonium sulphide, and citric acid. The chromium (if any) is converted into alkaline chromate by fusion with sodium carbonate and nitre; the mass is dissolved in water; and, without filtering, potassium chlorate and hydrochloric acid are added, and the solution is evaporated to dryness in the water-bath, keeping the chlorate in excess. The residue is redissolved in water; a slight excess of ammonium carbonate is added; the solution boiled till all smell of this salt is removed, then filtered, and mixed with excess of hydrochloric acid; and when the greater part of the chlorate is decomposed, a little alcohol is to be added and the chromium precipitated as before. The alumina obtained by precipitation with ammonium carbonate is apt to be contaminated by silica and lime (from the citric acid), from which it can be separated by dissolving in hydrochloric acid, evaporating to remove silica, redissolving in hydrochloric acid, and precipitating with ammonium carbonate, care being taken to remove all excess of carbonate by boiling.

Manganese. S. Peters (*Chem. News*, xxxiii. 35) estimates manganese in iron and steel by a colorimetric method. 0.1 gram of the metal is dissolved at boiling heat in 3 to 4 c.c. of nitric acid (sp. gr. 1.2); lead dioxide (0.2–0.3 gram) is then added, the liquid is boiled for two or three minutes and filtered; the filtrate is poured into a burette and diluted to 50–60 c.c.; and the tint of this liquid is compared with that of a solution of permanganate containing 0.01 gram manganese in a cubic centimeter. If the two have the same depth of colour, the necessary data for calculation are obtained.

For the estimation of manganese in *spiegeleisen* and *ferromanganese*, the two following methods are given by E. Riley (*Chem. Soc. J.* xxxii. 1–12).

1. *Direct Method.*—About a gram of finely comminuted *spiegeleisen* is dissolved in nitric acid (sp. gr. 1.2), and small quantities of potassium chlorate and hydrochloric acid are added to decompose the carbon-compounds produced by the reaction. The solution diluted to about a litre and neutralised with sodium or ammonium carbonate is then heated with sodium or ammonium acetate (preferably with the ammonium salt), the resulting basic ferric acetate is left to settle; the solution is filtered; the precipitate redissolved in hydrochloric acid; and the process repeated in order to ensure a complete separation of the iron and manganese. The united filtrates are evaporated to half a litre, and mixed after cooling with 2 to 4 c.c. of bromine and agitated; excess of ammonia is added; the liquid gently heated for about an hour, then boiled for five minutes; the precipitate is left to settle; the liquid is filtered; and the filtrate is evaporated and tested for manganese. Lastly the precipitate is dried and heated to redness for half an hour in a muffle or over a Bunsen burner, and finally over a gas blowpipe. It then consists of *manganoso-manganic oxide*, Mn^2O^4 .

Indirect Method.—About a gram of finely crushed *spiegeleisen* is dissolved in hydrochloric, or better in dilute sulphuric acid; the liquid is diluted with recently boiled distilled water; and the iron is estimated volumetrically with bichromate or permanganate; to the amount thus obtained 5 per cent. is added for carbon and impurities; and the difference is regarded as manganese. The result thus obtained is generally too low by 0.6 to 0.8 per cent., the error arising from the formation—during the dissolution of the iron—of oily hydrocarbons and soluble organic matter, which act more or less on the oxidising solution, thus rendering the amount of iron too high, and consequently that of manganese too low. The method however is for the most part sufficiently accurate for technical purposes, and it has the great advantage of being very expeditious, an hour being sufficient for its completion, whereas the direct method takes five or six hours. The indirect method may however be rendered much more exact, though at some sacrifice of time, by dissolving the *spiegeleisen* in nitric acid, evaporating to dryness, and heating the residue to destroy the carbon-compounds. The oxides of iron and manganese are then to be dissolved in hydrochloric acid, and the solution largely diluted with water, reduced with sodium sulphite, and titrated as before. The results of the indirect method, thus modified, agree very nearly with those of the direct method.

W. Galbraith (*Chem. News*, xxxiv. 47) dissolves 1 gram of *spiegeleisen* in nitric acid in a small round-bottomed flask, evaporates to dryness, and heats the residue for ten minutes at a cherry-red heat. A weighed quantity of ferrous or ammonio-ferrous sulphate is added, after cooling, together with a little dilute hydrochloric acid; the liquid is heated, with agitation; and when the whole is dissolved, the quantity of unoxidised iron is determined by titration with potassium dichromate. From this the

amount of manganese present may be calculated. Riley is of opinion that this method does not yield exact results.

Estimation of Manganese in Manganiferous Iron Ores.—These ores sometimes contain small quantities of baryta, zinc oxide, potash, soda, and silica. 1 gram of the ore, dried at 100° , is dissolved in hydrochloric acid, the silica separated by filtration, and the greater part of the free acid evaporated off. The solution is diluted to $\frac{1}{2}$ litre, left at rest for four hours, and treated with a few drops of sulphuric acid to precipitate the baryta; then diluted to 1 litre, mixed with ammonium acetate, neutralised with ammonia, heated to the boiling point, left to clarify, and filtered; and the precipitate, redissolved in hydrochloric acid, is again precipitated by ammonia after addition of ammonium acetate. The basic ferric acetate thus precipitated is left to settle, collected on a filter, and washed three or four times with boiling water containing a few drops of ammonium acetate. Lastly, the filtrate is evaporated to half a litre, mixed when cold with 2 to 4 c.c. bromine, and otherwise treated as above described for the analysis of spiegeleisen. The ignited manganoso-manganic oxide must be tested for barium, zinc, calcium, &c. Chlorine may be used instead of bromine for the oxidation of the manganese, but there is no advantage in this alteration of the mode of proceeding (Riley, *Chem. Soc. J.* xxxii. 12).

The following process for the analysis of manganiferous iron ores is given by A. Fimaro (*Gazz. chim. ital.* vii. 286). 2 or 3 grams of the finely powdered mineral are dissolved in hydrochloric acid, and the solution evaporated to dryness after adding a drop or two of nitric acid to peroxidize the iron; the residue is heated with a small quantity of hydrochloric acid, diluted, and filtered from the separated silica, which is ignited and weighed; the solution containing the iron and manganese is exactly neutralised with ammonia, and precipitated with a slightly acid solution of ammonium benzoate or succinate; and the precipitate, which contains the iron and alumina, is collected, washed first with water, then with dilute ammonia, and finally dried, ignited, and weighed. The iron and alumina in this precipitate may then be separated and determined in the usual manner. The manganese is precipitated as sulphide by sulphide of ammonium, and determined as manganoso-manganic oxide in the usual way. If the mineral contains copper or zinc, these must be removed by passing sulphuretted hydrogen through an acetic solution, previously to the precipitation of the iron. The magnesia and lime are determined in the filtrate from the manganese sulphide. This process is said to be especially valuable when the manganese is not in very minute quantity, and preferable to the separation by means of—
1. Ammonia and ammonium chloride. 2. Barium or calcium carbonate. 3. Sodium acetate and chlorine or bromine, or hypochlorite. 4. Lead oxide. 5. Conversion into sulphates.

On the separation of Iron and Manganese by means of Sodium Acetate, see also Stöckmann (*Zeitschr. anal. Chem.* xvi. 172) and Krämer (*ibid.* 334); also *Chem. Soc. J.* xxxii. 805.

Classen (*Berl. Ber.* x. 1316) separates iron from manganese, cobalt, nickel, and zinc, by treating the concentrated solution of the metals with a solution of potassium oxalate (1 : 6), and excess of strong acetic acid, whereby the oxalates of manganese, nickel, cobalt, and zinc are precipitated, leaving the iron in solution. The filtrate (with the washings) is concentrated on the water-bath, and rendered alkaline by sodium carbonate; the precipitate which forms is dissolved in concentrated oxalic acid; the solution precipitated with acetic acid as before; and the precipitate first obtained is washed with concentrated acetic acid, or a mixture of equal parts of acetic acid, alcohol, and water. It may still retain a trace of iron, which may be separated by a repetition of the process.

IRON METALLURGY. 1. **Cast or Pig Iron.** 1. *Chemistry of the Blast Furnace.*—*Temperature of the Blast.*—H. Valérius (*Bull. Acad. Roy. Belgique*, [2], xxxix. No. 4, April 1875) has calculated the temperature to which the blast must be raised in order to obtain the greatest heat in the furnace. By former experiments he had found that carbon burning in the open air produces a temperature of 1678° , half of it burning to dioxide, the other half to monoxide. Carbon monoxide in burning produces a temperature of 2231° C. In both cases it is assumed that the quantity of air supplied is such that its oxygen just suffices for complete combustion. When, however, carbon monoxide burns under this condition, only $\frac{1}{2}$ of it is burnt to CO_2 , the other $\frac{1}{2}$ remaining unaltered. The burning of CO in the air cannot raise the temperature higher than 2231° , as at higher temperatures cooling takes place in consequence of the dissociation of CO_2 . From these considerations, it is easy to calculate to what height the temperature of the blast must be raised, in order to obtain this maximum of temperature. Suppose that 1 kilogram of pure carbon is to be burnt; this will require 12 kilograms of air of the temperature x . Since now the

specific heat of air = 0.2375, the quantity of heat required to be added to the air, which is to be used for the combustion, will be $12 \cdot 0.2375 \cdot x$ heat-units. Now the products of combustion, consist of 1.83 CO₂, 1.166 CO, 6.99 N and 3 air; and as the specific heats of the first three are respectively 0.2169, 0.245 and 0.244, the rise of temperature produced in the air will be expressed by the fraction :

$$\frac{12 \cdot 0.2375 \cdot x}{\frac{1.85 \cdot 0.2169}{\text{CO}_2} + \frac{1.166 \cdot 0.245}{\text{CO}} + \frac{6.99 \cdot 0.244}{\text{N}} + \frac{3 \cdot 0.2375}{\text{Air}}} = \frac{2.85 \cdot x}{3.12}.$$

This temperature of the air is added to the temperature of combustion of the carbon in the air, so that the sum represents the maximum temperature, viz. :

$$1678 + \frac{2.85 x}{3.12} = 2231^\circ;$$

whence it follows that $x = 605^\circ$. In practice this amount is not sufficient, since the fuel burnt is not pure carbon; and hence it is that good results have been obtained by heating the air even to 800° . By the use of air at 600° , there is a saving of about $\frac{1}{5}$ of the carbon that would be required if cold air were used.

Use of Lignite in the Blast furnace.—Experiments on iron smelting with a mixture of coke and lignite are described by v. Frey (*Dingl. pol. J.* cxxvii. 71). It was found that 33 per cent. of the coke might be replaced by crude lignite (a poor variety from Lieschau) without any deterioration in the quality of the dark brown Bessemer iron produced in the furnace, and with a considerable saving of expense for fuel. The following table shows the composition of the iron made with coke alone, and with the mixture of coke and lignite :

from	Pig-iron smelted with :	Fe	Combined Carbon	Graphite	Si	Mn	S	P	Cu
Prevali	66.6 p. c. Fünfkirchen Coke	38.251	0.450	3.860	2.23	5.098	0.082	0.012	0.016
	33.3 " Lieschau Lignite								
	87 " Lime, White Ores								
Prevali	Coke	90.790	0.430	2.775	2.765	3.020	0.118	0.042	0.060
Kalán	25 p. c. Ostran Coke	—	—	—	up to 3.020	1.820 to 3.060	0.010 to 0.030	trace	—
	25 " Fünfkirchen Coke								
	25 " Hard Charcoal								
	25 " Crude Lignite								

The construction and working of a lignite blast furnace at Friedrichshütte in Bohemia are described by A. Kerpely (*Dingl. pol. J.* cxxix. 322; *Jahresb. f. Chem.* 1876, 1060).

Use of Quick Lime in the Blast furnace.—The introduction of quick lime into the furnace in place of the raw limestone generally used might be expected to effect a considerable saving of fuel, seeing that a large quantity of heat is expended in expelling the carbon dioxide from the raw limestone, and further that a certain quantity is absorbed during the reduction of this carbon dioxide to monoxide. The actual saving effected is, however, less than that which is indicated by theory. Experiments have indeed shown that the use of burnt lime in the smaller blast furnaces is attended with a somewhat greater production, a better quality of iron, and also at times with a trifling saving of fuel, but in the larger and newer furnaces this is not the case. The reduction by carbon monoxide of many easily reducible ores begins at 200° , and the products of this reduction are carbon dioxide, iron, and a certain quantity of carbon. Carbon dioxide also, at a certain temperature, is reduced by carbon to monoxide. At 410° the carbon dioxide begins to reoxidise the iron reduced at the lower temperature, and this oxidation increases with the rise in temperature, so that at a bright red heat a mixture of carbon dioxide and monoxide in equal volumes will extract from sesquioxide of iron only one-third of its oxygen, whilst metallic iron at the same temperature will take up from such a mixture two-thirds of the oxygen which it would contain as sesquioxide. By the use of burnt lime the heat in the furnace is certainly increased, and the presence of this heat is made known by a rise in the temperature of the escaping gases. This increase in temperature, however, induces a greater formation of CO in proportion to CO₂, perhaps through the oxidising power of the latter being increased, and, therefore, more carbon monoxide being necessary for the reduction, or perhaps through the carbon dioxide being more easily reduced by the carbon. Whichever may be the true explanation, the result remains the same, viz., an absorption of heat, which means a waste of fuel, so that the gain on the one hand is neutralised by a loss on the other. (I. L. Bell, *Engineering*, Sept. 1875, p. 203; *Dingl. pol. J.* cxxviii. 260.)

Composition of Gases and Slags from the Alfreton Blast-furnace.

	Carbon	Hydrogen	Oxygen	Nitrogen	Silica	Alumina	Potash	Limestone	Magnesia	Iron
Coal	292.42	21.67	65.01	0.70	10.18	—	0.27	—	—	—
Iron ore	—	—	75.89	—	108.23	27.46	3.11	14.74	13.40	177.11
Limestone flux	19.89	0.26	54.99	—	—	1.36	—	92.48	1.02	—
Air	—	—	316.24	1658.27	—	—	—	—	—	—
Moisture	—	1.52	12.22	—	—	—	—	—	—	—
Total raw material	312.31	23.46	524.35	1658.97	118.41	28.82	3.38	107.22	14.42	177.11
Deducting iron	5.60	—	+ 3.20	—	{ Si : 2.80 } { O : 3.20 }	—	—	—	—	131.60
Deducting slag	306.71	23.46	527.55	1658.97	112.41	28.82	3.38	107.22	14.42	45.51
Gases	306.71	23.46	527.55	1658.97	112.41	28.82	3.38	107.22	14.42	45.51
Percentage composition of the gases	16.00	1.22	27.53	55.25	—	—	—	—	—	—
Percentage composition of the slags	—	—	—	—	36.24	9.28	1.08	34.26	4.60	14.54

On Reiser's proposed method of using gaseous fuel and mineral fuel from the more recent formations, in blast furnaces, see *Dingl. pol. J.* cccviii. 176; *Jahresb. f. Chem.* 1875, 1023.

Gases and Slags.—W. Kent (*Engineering and Mining Journal*, April 1875, p. 228; *Dingl. pol. J.* cccviii. 332) has calculated the composition of the gases and slags from blast furnaces, basing his calculation on the obvious principle that whatever is introduced into the furnace must leave it in some form or other, either as gas, or as crude iron, or as slags. The table on p. 1106 shows the result of the calculation for the Alfreton blast furnace, from data furnished by Dr. Percy.

Formation of Chlorine-compounds in Blast-furnaces.—In several German iron works, viz. the Concordia works at Benndorff, the Sophia works at Wetzlar, and the Main-Weser works at Lollar, much damage has been done to the furnaces by the formation of chlorine-compounds. At the Concordia works it was noticed that the iron plates of the furnace were destroyed, and that the pumice placed in compartments in the throat of the furnace to absorb the gases, had assumed a yellowish-brown colour from the formation of ferric chloride, and partly caked together. Fused salts, chiefly potassium chloride, likewise exuded through the walls of the furnace. Similar observations were also made at other works. Now chlorides do not occur in iron ore or in limestone, and they are not likely to be derived from the building material of the furnace. The source of them must therefore be looked for in the coke with which the furnaces were fed; and in fact the liquid obtained by lixiviating an average sample of 35 kilos. of this coke gave by analysis:

43.54 grms. NaCl	=	·1209	per cent. on the coke.
1.38 " KCl	=	·0038	" " "
·72 " MgO.SO ³	=	·0020	" " "
9.76 " KO.SO ³	=	·0271	" " "
3.92 " KS	=	·0108	" " "
9.58 " CaS	=	·0266	" " "
68.90 grms. salts	=	·1912	per cent. on the coke.

Consequently a furnace consuming daily about 50 tons of coke would at the same time receive 60.47 kg. NaCl and 1.91 kg. KCl, which together would be capable of yielding 38.73 kg. HCl, so that the decomposition of only a small proportion of these chlorides would be sufficient to account for the damage done to the furnaces.

The analysis above quoted agrees moderately well with those of many lime-springs, the only difference being that the former exhibits a larger proportion of sulphates. Now such waters are known to exist in the Westphalian coal-districts, and their use for quenching the coke would account for the presence of chlorides therein; and, in fact, since the use of these waters at the Concordia works has been discontinued, the destructive action above described has no longer been noticed (Chr. Meineke, *Dingl. pol. J.* cccvii. 217).

Analysis of White Fumes from a Blast-furnace near Longwy.—The ores used in this furnace are ferruginous oolite, with a matrix of clay-slate. They are reduced with coke, and with a blast heated to 500°–600°, in order to obtain black or grey pig-iron, like that from Scotch furnaces. Owing to the high temperature of the blast, a dense white smoke is evolved which incrusts the walls of the work. The portion of this crust which is soluble in water consists largely of potassium sulphate, but no sulphide; but the insoluble part evolves sulphuretted hydrogen on treatment with an acid. On analysis, the deposit was found to have the following composition:

Portion soluble in Water.

K ² SO ⁴	K ² CO ³	KCl	Soluble SiO ²	
37.82	3.90	1.52	0.12	= 43.36

Insoluble portion.

SiO ²	CaO	Al ² O ³	FeO	MnO	MgO	S	
22.98	15.88	9.62	4.00	0.16	0.36	not det.	= 53.00
Hygrometric Water							= 3.20
							99.56

The following is the percentage composition of the insoluble portion (exclusive of sulphur) compared with that of the slag:

	SiO ²	CaO	Al ² O ³	FeO	MnO	MgO	K ² O	S	H ² SO ⁴	
Insoluble.	43.3	30.0	18.1	7.6	0.3	0.7	—	—	—	= 100
Slag.	33.0	43.7	14.6	3.6	—	1.9	1.7	0.7	0.2	= 99.4

As the slag is more basic than the insoluble portion of the fume, it would appear that the latter is mixed with free silica; and on examination, it was found to contain fibrous silica, probably evolved as silicon sulphide, which, on exposure to moist air, was converted into fibrous silica. The potassium sulphate was probably due to the oxidation of volatilised potassium sulphide (L. Gruner, *Compt. rend.* lxxiii. 559).

Limit of the Carburation of Iron.—M. Boussingault (*Compt. rend.* lxxx. 850) infers, from experiments made by himself and by others, that the highest amount of carbon that iron can take up is 4.1 per cent., answering to the formula Fe^{C} . This compound may exist in the fused state, but undergoes dissociation, partly at least, on cooling, as shown by the appearance of graphite in the mass, so that the solidified iron may be regarded as a mixture of Fe^{C} with free iron and free carbon. The transformation of grey into white cast-iron appears to be due simply to the manner of cooling the metal, rapid cooling producing the white, and slow cooling the grey variety.

2. Silicon in Pig-iron.—The form in which silicon exists in pig-iron has been investigated by E. H. Morton (*Chem. News*, xxix. 107). When the iron is dissolved in a dilute acid, the silicon remains in the form of silica; and the same result is obtained on heating Bessemer pig with fuming sulphuric acid or with iodine in sealed tubes, the air of which has been previously displaced by hydrogen or carbon dioxide, the formation of silica being attended, in the one case, with the formation of sulphur dioxide, in the other, when iodine is used, with deoxidation of carbon dioxide. The residue obtained on treating pig-iron with fuming sulphuric acid consisted of crystallised and amorphous silica, but did not contain a trace of free silicon; neither was any silicon found in the residue left when the pig was dissolved in hydrofluoric acid. From these results Morton infers that the silicon in pig-iron is chemically combined, not merely mechanically mixed. When siliceous iron is decomposed by acids or by iodine, the silicon appears to be oxidised at the moment of liberation; free silicon is not affected by these oxidising agents. When pig-iron containing silicon is heated in a stream of hydrogen, the silicon is volatilised; and by subsequently passing the gas into dilute potash-solution, acidulating this liquid, evaporating to dryness, and estimating the silica in the usual way, it was found that a pig-iron containing 4.612 per cent. silicon yielded to hydrogen 0.344 per cent., while a second specimen containing 4.704 per cent. Si yielded to hydrogen 0.494 per cent. Free silicon does not unite with hydrogen, so that in this case also it appears that a compound of iron and silicon is decomposed by the hydrogen.

Investigations on iron rich in silicon have been made by Troost a. Hautefeuille (*Ann. Min.* 1874, iv. 1). Iron of this description is employed in the Bessemer process, not only because it determines a higher temperature in the converter, but because the refining of it is not attended with so great a loss by sparkling as is the case in the refining of ordinary pig-iron. The emission of sparks is occasioned chiefly by the escape of gases contained in the pig-iron, but siliceous iron is very poor in gases, and when refined in a current of air, presents an appearance similar to that of lead in cupellation.

Pig-iron, heated in an apparatus made of refractory silicates, always yields carbon monoxide, and at the same time takes up silicon; this shows that iron carbide has the power of decomposing silicates and separating the silicon from them:

	Si	C
A pig-iron originally containing	0.21	5.32 per cent.
" contained, after 48 hours heating in a porcelain crucible	0.87	5.20 "
" 24 " " " gaize " "	1.07	3.20 "
Globules of " metal which penetrated into the gaize contained	3.40	—
A cast-steel originally containing	0.10	1.54 "
" contained, after 24 hours heating in a hessian crucible .	0.26	0.24 "
" " " " " gaize " "	0.80	0.70 "

These results show that, to fuse iron without introducing silicon into it, the fusion must be effected in vessels of lime or magnesia. On the other hand, iron rich in silicon gives up a certain portion of that element when heated in a lime crucible.

In the blast-furnace the absorption of silicon takes place only after the combination of the iron with the carbon; that is to say, it begins in the boshes of the furnace, and is completed in the hearth. It is especially from the silicates of the alkali-metals that iron takes up the largest quantity of silicon. By fusing together crude potash, charcoal, iron filings, and silica, a regulus was obtained containing 15.16 per cent. silicon and 2.94 per cent. carbon.

3. Manganiferous Cast iron.—The varieties of these alloys, containing not more than about 26 per cent. manganese, are known as *Spiegeleisen*; those with higher proportions of manganese are named *Ferromanganese*. The following

tables (p. 1110) contain analyses of spiegeleisen. Table I. by E. Riley (*Chem. Soc. Jour.* xxxii 7).—Table II. analyses of Carniola spiegeleisen by the Carniola Company at Laibach, to which are appended determinations of the carbon by Riley.

According to Riley's analysis in Table I., the percentage of carbon increases on the whole with that of the manganese. The analyses by the Carniola Company show rather the contrary result; but Riley's analyses of the same spiegeleisens likewise show an increase of carbon on the whole from about 15 to 50 per cent. manganese, though there is a decrease in the carbon between the samples containing 35 and 40 per cent. manganese. In the ferromanganese containing 73 per cent. Mn, the percentage of carbon is higher than in any of the spiegeleisens. (For methods of analysis, see pp. 1103, 1104).

Spiegeleisen is largely produced in Germany, Russia, and Sweden, and the ores from which it is obtained are of very different and peculiar characters. In Germany it is produced solely from spathic iron ores containing manganese; in Russia from manganese oxides containing iron; and in Sweden by fluxing a mixture of knebelite and manganiferous garnet (combined silicates of iron and manganese). An important point with reference to these ores is that, if the iron and manganese oxides are not in actual combination as carbonates or silicates, they are in a state of very intimate mixture: for whenever pure manganese ores are added to the blast furnace mixture, with the view of obtaining spiegeleisen rich in manganese, the result is always a failure, only a small fraction of the added manganese combining with the iron, while the greater portion is carried off in the slag. To produce pig-iron rich in manganese, the manganese must therefore be added to the mixture in the form of a compound containing iron; the reduction process is thereby facilitated, since a mixture of the oxides of manganese and iron is more easily reduced to the metallic state, and is thus enabled to unite with the iron of the charge. With manganese alone there is a great tendency for this metal to pass into the slag as a silicate, from which it cannot be profitably recovered. To prevent this, the heat should be as great as possible, and the reducing power of the furnace almost complete. The oxides of manganese are much less easily reduced, and require more time and a much higher temperature than those of iron. In the production of spiegeleisen, the following points should be especially observed:—

1. The manganese ore used should contain a large proportion of iron, in order to secure the easy reduction of a large portion of manganese.
2. The furnace charge should be basic; *i.e.*, an excess of limestone, or, better, of burnt lime, should be used.
3. The draught of the furnace should be much slower than in the ordinary process, in order to give more time for the reduction of the manganese.
4. The furnace temperature should be as high as possible, the air employed as hot as possible; and as coke bears a stronger pressure of air and develops a greater heat, it is preferred to wood charcoal in this process.

At Filipstad, in Sweden, spiegeleisen has been made by using native oxides of manganese, especially Hausmannite, which contains 72 per cent. manganese. The iron produced contained only 4 per cent. manganese, the excess of the metal passing away in the slag.

The ores employed in Germany for the manufacture of spiegeleisen are found in veins of the Devonian formation, on the east bank of the Rhine. They are spathic ironstones, which consist of carbonate of iron intimately mixed with carbonate of manganese. They further contain more or less copper and iron pyrites, with traces of galena and zinc blende, and frequent occurrence of quartz. Analyses of the products of three different mines gave the following results:—

	Stahlberg	Kirschenbaum	Huth
	p. c.	p. c.	p. c.
Iron	41.70	42.58	42.21
Manganese	8.16	6.46	8.70

The well-known foliated texture of spiegeleisen depends more upon the amount of carbon contained in it than upon the amount of manganese. This structure is also better developed if the iron, after running off, is covered over with slag, so as to allow it to cool more slowly.

The following analyses show the percentage composition of spiegeleisen manufactured with coke in Germany.

	C	Si	S	Cu	Mn	Fe
(1)	4.129	0.458	0.015	0.210	8.706	85.929
(2)	5.04	0.41	0.08	0.16	7.57	86.74

(Forbes, *Journal of the Iron and Steel Institute*, Feb. 1872).

TABLE I. *Analyses of Spiegeleisen (Riley).*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Iron . . .	88.378	86.713	85.507	83.777	81.111	80.581	79.358	76.361	74.602	74.980	74.745	73.886	72.775	71.606	69.180
Manganese . . .	6.984	8.448	9.856	11.782	13.689	14.770	15.648	18.215	19.406	19.768	20.318	20.423	22.560	22.680	26.073
Carbon . . .	4.176	4.071	4.501	4.538	4.443	4.164	4.519	4.758	4.358	4.402	4.603	4.633	4.808	5.133	5.032
Silicon245	.629	.248	.041	.476	.096	.426	.375	1.546	.894	.637	.888	.476	.539	.169
Sulphur100	.039	.041	.010	nil.	trace	.021	traces	.016	.037	.017	.022	nil.	.019	nil.
Phosphorus037	.483	.098	.084	.212	.365	.098	.059	.283	.085	.117	.034	.072	.066	.089
Copper424	.102	trace	.015	.080	trace	.042	traces	—	trace	—	—	.024	—	traces
Total of elements other than iron and manganese . . .	100.344	100.485	100.251	100.247	100.011	99.976	100.112	99.763	100.211	100.166	100.437	99.916	100.715	100.043	100.533
	4.982	5.324	4.888	4.688	5.211	4.625	5.106	5.187	6.203	5.418	5.374	5.607	5.380	5.757	5.280

Mean of 14 analyses, omitting No. 9, 5.20.

TABLE II.—*Carniola Spiegeleisen.*

	1	2	3	4	5	6	7	8
Iron . . .	78.01	73.50	68.71	*63.27	69.00	53.39	48.17	43.85
Manganese . . .	15.41	20.47	25.10	30.51	34.90	40.28	45.62	49.98
Carbon . . .	5.20	4.60	4.97	4.96	4.98	4.90	4.80	3.73
Silicon72	.90	.80	.79	.85	.86	.91	1.08
Sulphur04	.03	.02	.02	.03	.02	.02	—
Phosphorus33	.23	.30	.28	.20	.29	.25	.22
Copper . . .	—	—	—	.01	.01	.01	—	.02
Aluminium02	—	.01	.05	.08	.06	.06	.01
Calcium10	.09	.07	—	—	—	—	—
Arsenic . . .	—	—	—	—	—	—	—	—
Carbon (Riley) . . .	99.83	99.82	99.98	99.89	99.95	99.81	99.83	90.79
	4.164	—	—	4.642	4.780	4.473	5.065	4.297
	—	—	—	—	—	4.483	—	4.364
Carbon per cent. in ferro-manganese (73 per cent. manganese)					I	II	Mean	
					6.324	6.253	6.288	

The following are analyses of the best kinds of German spiegeleisen imported into New York in the years 1868, 1869, and 1873 (*Dingl. pol. J.* ccxii. 350):—

	1868		1869		1873	
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Iron	85.570	84.455	84.122	84.869	—	—
Manganese	9.142	10.625	10.568	10.223	11.130	10.22
Copper	0.032	0.034	0.036	0.031	0.279	0.20
Cobalt and Nickel	0.005	0.005	0.004	0.002	—	—
Silicon	0.068	0.368	0.286	0.384	—	—
Carbon	5.048	4.304	4.907	4.461	—	—
Sulphur	—	0.002	—	0.001	—	—
Phosphorus	0.037	0.044	0.014	0.027	0.039	0.06
Aluminium	0.082	0.045	0.032	0.012	—	—
Calcium	0.015	0.016	0.021	—	—	—

The New Jersey Zinc Company manufactured in 1874 from three furnaces 4,070 tons of spiegeleisen having the following composition (*Dingl. pol. J.* ccxvii. 154):—

Fe	Mn	Si	C	P
83.250	11.586	0.367	4.632	0.166
83.22	11.67	0.99	4.02	0.19

The function of manganese in iron metallurgy is explained by Troost & Hautefeuille (*Compt. rend.* lxxxi. 265) as follows: Manganese unites readily with the impurities of iron, giving rise to compounds whose formation is attended with the evolution of a quantity of heat greater than that which is evolved in the formation of the corresponding iron-compounds. These manganese-compounds unite with oxygen more readily than iron-compounds, manganese even taking oxygen from the oxides of iron. At the same time the manganese in oxidising develops an amount of heat which greatly facilitates the formation of slag.

On the Decarburization of Spiegeleisen, see W. Raymond (*Dingl. pol. J.* ccxx. 60; *Jahresb. f. Chem.* 1876, 106).

4. *Manufacture of Pig-iron containing Manganese and Phosphorus* (Le Chatelier, *Dingl. pol. J.* ccxvi. 342).—Near Liège there occurs an iron ore which yields a pig-iron containing 4 per cent. of phosphorus, and when this ore is mixed with a manganiferous iron ore, found near Nassau, containing 15 per cent. manganese and 33 per cent. of iron, a pig is obtained, which easily gives up the phosphorus in puddling. At Grovigné, 1,000 kilos. of coke, 1,500 kilos. of ordinary, and 500 kilos. of manganiferous ore are used for an iron containing manganese; and for ordinary pig-iron, 1,000 kilos. of coke, 850 kilos. of lime, and 2,500 kilos. of ordinary ore. Three different sorts of pig-iron are manufactured, one containing more than 6 per cent. of manganese, which, when broken across, shows mirror-facets; another with 3 to 6 per cent. of manganese, but with facets so small as hardly to be visible; and the third contains less than 3 per cent. of manganese. The slags are green in the interior, and brown on the outside. They contain $\frac{1}{2}$ to $\frac{3}{4}$ of the amount of manganese in the ore. If much lime is added, a white pig is formed, rich in manganese.

The following are analyses of these pig-irons and their slags:

	Pig-iron							
	a	b	c	d	e	f	g	h
C	3.5	—	—	6.29	2.25	2.12	—	—
Si	1.0	0.6	—	0.7	0.98	0.97	0.213	0.376
S	—	not determined			0.009	0.05*	0.04	—
P	1.6	1.09	1.46	—	1.20	0.52	1.84	2.804
Mn	2.3	3.04	1.60	5.27	2.65	2.73	0.279	—
Cu	—	—	—	—	0.03	—	—	—

a. Grevigné; b, c, d. Ougrée; e, f. Dolhain; g, h. Espérance.

	Slags			
	a	b	c	d
SiO ₂	32.75	35.00	39.00	38.00
CaO	36.00	45.00	40.00	41.00
MgO	9.77	—	—	—
Al ₂ O ₃	17.82	13.00	12.00	14.60
FeO	0.93	3.76	2.17	2.17
MnO	1.21	0.50	2.00	1.50
S	0.74	0.59	—	0.45
P ₂ O ₅	—	0.36	1.625	0.20

a. Slag from pig-iron containing 6 per cent. of manganese; b, c, d. Slag from Espérance.

On the Conversion of this Pig-iron into Wrought Iron and Steel, see p. 1116.

5. *Iron containing Copper*.—Wrought iron containing some tenths per cent. of copper is known to be red-short; nevertheless, some of the best irons from Siberia have been found to contain from 0·01 to 0·03 per cent. of copper. Some specimens of steel contained 0·2 per cent., but the steel was not brittle, and had been used with success for the manufacture of steel axles. Specimens of cast iron from the blast furnaces of the South Ural mountains showed that the presence of copper in cast iron may amount to a higher percentage than in steel or iron, without altering the quality of the metal. The following is the composition of this peculiar sample of cast iron:

Fe	Cu	Sn	Co	Si	Ni	C	Mn
83·514	8·123	1·252	0·501	0·952	0·125	3·001	2·312 = 99·780

(S. Kern, *Chemical News*, xxxiv. 78).

Leithner (*Dingl. pol. J.* ccxi. 349) utilises the residues from the cupriferos pyrites which have been used in sulphuric acid works to generate sulphurous acid, for the preparation of a cupriferos iron to be employed in the precipitation of 'cement-copper.' The burnt pyrites is freed as far as possible from sulphur by a second roasting close to the blast-furnace, then mixed with lime and smelted. The cupriferos pig-iron thus obtained yields up its copper to the solutions from which it precipitates the copper.

6. *Malleable Cast Iron* (2nd Suppl. 696).—The chemical changes which take place in the manufacture of this kind of iron by heating ordinary cast iron in a bed of smithy scales, have been examined by Russell Davonport (*Mechanics' Magazine*, 1872, p. 392; *Dingl. pol. J.* cvii. 51). The samples examined were a quarter of an inch thick, and were analysed both before ignition and after each of two heatings. The following numbers represent mean percentages:

Casting No 1	Before ignition	After first ignition	After second ignition
Silicon	0·445	0·438	0·449
Phosphorus	0·315	0·327	0·315
Manganese	0·529	0·585	0·525
Sulphur	0·059	0·067	0·083
Total carbon	3·43	1·51	below 0·10
Casting No. 2			
Silicon	0·585	0·614	0·614
Phosphorus	0·280	0·290	0·295
Manganese	0·585	0·616	0·575
Sulphur	0·105	0·147	0·162
Total carbon	3·48	0·43	below 0·10

These numbers show that the proportions of silicon, phosphorus, manganese, and sulphur in pig iron are not essentially altered by ignition; the slight increase of sulphur is derived from the fuel. The carbon is wholly removed by heating the iron to redness in contact with ferric oxide, the burning out of the carbon proceeding from without inwards. After the first heating the castings exhibit a black nucleus surrounded by a white crust nearly free from carbon. In the dark nucleus (technically called the 'heart') graphite was recognised, although the pig-iron was originally free from it. After the second ignition the entire ingot had become white. Many of the castings after ignition were extremely brittle, and exhibited a coarsely crystalline texture; nevertheless they were not found to differ chemically in any respect from good iron.

7. *Solution of Gases in Cast Iron*.—J. Parry (*Amer. Chem.* vi. 107) finds that grey cast iron absorbs hydrogen to the amount of 20–22 times its bulk. On ignition in a vacuum, the hydrogen is given off, together with CO and CO₂. When volatile metals (zinc, cadmium, bismuth, magnesium, and even cobalt) are heated in a vacuum with iron, their vapours are taken up by the iron. On again heating the iron in a vacuum, the volatile metal is given off and deposited as a sublimate on the side of the tube.

Parry (*ibid.* iv. 254) has also examined the gases absorbed by spiegeleisen, white and grey pig-iron, bar-iron, and steel during the processes of manufacture. By heating these several forms of iron in the vacuum of a Sprengel pump, it was found that:

- 50 grams of spiegeleisen yielded in three hours 12 c.c. gas at 15° and 760 mm.
- 50 grams white pig gave in 6½ hours, 13 c.c. gas.
- 37 grams of bar-iron gave in two hours, 9·4 c.c. gas.
- 4·75 grams grey pig gave in two hours, 15·81 c.c. gas.
- 10 grams steel gave in two hours, 18·4 c.c. gas.

Percentage Composition of the Gases.

	CO ^a	CO	H	N
From Spiegeleisen	0·942	17·87	81·105	—
„ White pig	6·800	2·32	84·000	6·88
„ Bar iron	9·920	34·262	54·100	1·718
„ Grey pig	1·600	5·200	89·700	3·250
„ Steel	16·550	24·352	52·610	6·488

The experiments of Troost a. Hautefeuille (*Compt. rend.* lxxvi. 482, 562) on the action of iron carbide on siliceous compounds (p. 1110) show that, in order to study the absorption of gases by iron, it is necessary to employ a vessel free from silicon; they therefore employed vessels made of carbon.

Cast iron raised to a high temperature in a carbon boat in an atmosphere of hydrogen undergoes tranquil fusion; there is no disengagement of gas and no projection of the metal. But if, after it has remained for some time in this atmosphere, the pressure of the hydrogen be rapidly diminished, the disengagement of gas is rendered evident by the projection of globules of metal and particles of graphite, and if the temperature be allowed to fall at the same time, the metal solidifies during the disengagement of gas, and the surface of the ingot is rough. The solubility of hydrogen in cast iron is much diminished by the presence of phosphorus or silicium (especially the latter) in the metal. Carbon oxide is much less soluble than hydrogen in cast iron, more especially in highly carburetted iron.

These results were confirmed by extracting the gases dissolved or enclosed in pig-iron. A cylinder of the metal weighing 500 grams heated to 800° in a vacuum gave off in 190 hours 16·7 c.c. of gas consisting of

Carbon dioxide	Carbon oxide	Hydrogen	Nitrogen
0·6	2·8	12·3	1·0

The greater part of the carbon oxide was disengaged in a few hours, while the hydrogen was much more forcibly retained.

The same cylinder of cast iron was afterwards heated to 800° for 48 hours under a pressure of 770 mm. (1) in hydrogen, and (2) in carbon oxide, and after each operation placed in a vacuum for 170 hours. The gases extracted in the two cases were—

	Carbon oxide	Hydrogen	Nitrogen
(1.)	1·1	44·0	1·5 = 46·6 c.c.
(2.)	14·7	1·5	0·7 = 16·9 „

Hence the order of solubility is the same as in the fused metal.

To ascertain the effect of different proportions of carbon in the metal on the solubility of the gases, comparative experiments were made with cast steel and soft iron. Cylinders of these metals, each weighing 500 grams, when heated to 800° in a vacuum, gave off the following gases:

	Carbon dioxide	Carbon oxide	Hydrogen	Nitrogen
Cast steel	0·05	1·4	0·5	0·25 = 2·2 c.c.
Soft iron.	2·20	10·8	4·4	1·1 = 18·5 „

These cylinders were heated to 800° (1) in hydrogen, and (2) in carbon oxide, and afterwards placed in a vacuum, as in the case of the cast-iron cylinder. The gases extracted were—

		Carbon oxide	Hydrogen	Nitrogen
From cast steel	{ (1.)	0·9	6·4	0·5 = 7·8 c.c.
	{ (2.)	2·0	0·8	0·4 = 3·2 „
From soft iron	{ (1.)	0·6	10·0	3·3 = 13·9 „
	{ (2.)	13·7	0·2	0·1 = 14·0 „

Steel retains the last traces of hydrogen much more forcibly than cast iron, notwithstanding that when saturated with the gas it gives off a portion at the ordinary temperature, in this respect resembling palladium. Soft iron retains carbon oxide more forcibly than it retains hydrogen, contrary to what is observed with cast iron and steel.

The evolution of gases from pig-iron has also been examined by A. Ledebur (*Chem. Centr.* 1873, 810), who attributes it to three causes: 1. Gases absorbed by the iron in the blast-furnace are given off in consequence of the reduction of pressure which takes place when the furnace is tapped. An alteration in the constitution of the metal during cooling may also give rise to the escape of dissolved gases. The greater the proportion of graphite in pig-iron, the smaller is the quantity of gas which it gives off. Iron rich in carbon takes up chiefly gases containing a large proportion

of hydrogen; iron poor in carbon, especially in combined carbon, takes up chiefly gases in which the carbon predominates. 2. Evolution of gases also takes place in consequence of the contact of the melted iron with the air. The movement observed on the surface of the cooling iron is well known to be due to oxidation, a crust of ferroso-ferric oxide, silica, and oxides of manganese forming on the surface, breaking up, and being continually reproduced. This very basic slag may act upon the fused carburetted iron in such a manner as to give rise to the formation of carbon oxide. 3. Gases may be produced by the action of the fused iron on the sides of the mould. Even very carefully dried moulds contain small quantities of water, which is converted into vapour as the iron runs into the mould, and the steam passing through the molten iron gives rise to the formation of hydrogen, hydrocarbons, and hydrogen sulphide. The presence of this last gas is shown by the frequently observed occurrence of sulphur dioxide in the combustion of the gas which escapes from the iron.

Gases from Spiegeleisen.—This alloy, in flowing from the blast-furnace, gives out a much larger quantity of gas than ordinary pig-iron. The latter runs into the channels with vivid sparkling, and gives out only a few gas-bubbles in solidifying, whereas spiegeleisen appears to be covered with a film of gas, and gives out a large quantity at the moment of solidification. The gas burns like hydrogen, not like carbon dioxide. The appearance just described may be imitated by slowly fusing 200 grams of spiegeleisen in a lime crucible under the oxyhydrogen flame, then adding to the very hot bath 100 grams more, and removing the cover from the crucible as soon as this latter quantity is melted. In this case also, the shining metal-bath appears to be covered with a veil of gas, which may most readily be seen by placing the eye on a level with the specular surface of the metal. Gas-bubbles are then seen to escape from time to time from the metal, and for a moment increase the height of the flame. At the moment of solidification, the metal spits and gives off a considerable quantity of hydrogen. Spiegeleisen, after solidification, retains a much larger quantity of gas than ordinary pig-iron. 500 grams of the two heated in a vacuum to 800° gave:

	Pig-iron	Spiegeleisen
Carbon Dioxide	0.6 c.c.	0.0 c.c.
„ Monoxide	2.8 „	0.0 „
Hydrogen	12.3 „	27.0 „
Nitrogen	1.0 „	2.5 „
	<hr/> 16.7	<hr/> 29.5

The carburetted manganese obtained by reduction of the oxide by charcoal in a lime crucible, absorbs, when heated to redness in a flame of hydrogen, a larger quantity of this gas than iron containing an equal proportion of carbon. Hence it appears that manganese increases the capacity of iron for absorbing hydrogen, but diminishes its power of absorbing carbon monoxide (Troost & Hautefeuille, *Compt. rend.* lxxx. 909).

8. *Absorption of Heat by Pig-iron, Slags, and Steel at High Temperatures.*—The following numbers denote units of heat absorbed by a unit-weight of the substance; they were determined with a water-calorimeter, and represent minima, inasmuch as small losses of heat were unavoidable. 1. The several varieties of grey pig, as they run from the furnace, take with them only 280 to 285 heat-units, but while in the hearth they often contain from 300 to 310 units. 2. White pig under the same circumstances contains 20 units less. 3. Grey pig at its solidifying point contains 244 to 245 units, and immediately after solidification 221 to 222 units. 4. White pig at its solidifying point retains 225 to 235, and immediately after solidification 192 to 203. The several varieties of white pig have therefore a latent heat of 32 to 34 units, the grey only 23 units. 5. The slags contain $\frac{1}{10}$ as much heat as the iron, in the case of grey iron therefore 500, and in that of white iron 450 heat-units at the moment of tapping. 6. The latent heat of the slags is about 50 units. 7. Bessemer steel obtains by refining 30 heat-units more than pig-iron; fused steel often contains only 300 units. 8. The melting points of these varieties of iron and steel, as determined by Gruner, agree with those observed by Pouillet:

White pig-iron melts at	1050°–1100°
Grey siliceous pig-iron	1200°
Cast steel	1350°–1400°
White pig-irons running from the furnace have a temperature of	1250°–1300°
Grey pigs have a temperature of	1350°–1450°
Bessemer steel attains in the converter, at the moment of refining, a temperature of at least	1500°

(L. Gruner, *Ann. Min.* [7], iv, 224; *Dingl. pol. J.* ccxii. 527).

II. Wrought Iron. 1. Refining of Pig-iron.—A. Warner purifies pig-iron by subjecting it in the fused state to the action of a mixture of soda (sodium carbonate) and lime, using for each 1 per cent. of silicon to be removed, 20 kg. soda and an equal quantity of lime to a ton of iron. The lime being divided and distributed by the melting soda comes into intimate contact with the iron, and abstracts its silicon and sulphur. The action, which is energetic, lasts for twenty to thirty minutes, and two slags, consisting of silicates and sulphides, collect on the surface, below which the iron is tapped off. Iron thus refined contains only 0.04 per cent. sulphur and 0.10 to 0.14 silicon (*Dingl. pol. J.* cexvi. 490; *Engineering*, 1875, 132).

According to a later communication by E. Rigo (*Dingl.* cexviii. 125), Warner endeavours to effect the removal of silicon and sulphur by means of various mixtures of sodium carbonate and infusible substances. He uses: *a.* 2 pts. by weight of soda and 3 pts. of ferric oxide; 1 ton of pig-iron of 1 per cent. silicon requires 40 kilos. of the mixture — *b.* 1 pt. of soda and 2 pts. of oxide of manganese, 40 kilos. being required for 1 ton — *c.* 3 pts. of soda and 2 pts. of slaked lime; 1 ton of iron requires for every per cent. of silicon 38.5 kilos. of the mixture — *d.* 1 pt. soda and 2 pts. of fluor spar. This flux, however, cannot in general be recommended, though it answers well in special cases. Sodium carbonate, owing to its price, is added only in quantity absolutely necessary to obtain the desired object of bringing the action of the cheaper and specially refining agents into full operation.

2. Puddling.—A report on the progress of Mechanical Puddling (*2nd Suppl.* 697) has been published by P. Tunner (*Dingl. pol. J.* cexiii. 123). Riley a. Henley have adapted a principle, first laid down by J. v. Ehrenwerth, to the construction of a mechanical puddling furnace, in which a horizontal circular chamber revolves round a vertical axis under an arch similar to that of the ordinary puddling furnace. A great improvement in this furnace has been made by Pernot, who inclines the circular chamber towards the working door in such a manner that during the rotation part of the inclined hearth remains uncovered by the iron and slag. This part of the movable hearth, which projects into the hot air-stream, is subjected to powerful oxidation, but the oxidised products are immediately taken up by the bath of metal, slag, &c. With Pernot's furnace, the stirring, or puddling, properly so called, is performed by machinery, but the bolting up is effected in the ordinary way. At the works of Petin a. Gaudet in St. Chamond, a furnace thus constructed yielded in a week (with eleven 12-hour shifts), 500 centners of puddled iron, whereas an ordinary hand-puddle furnace yields only 240 centners. 1000 kg. wrought iron were produced from 1030 kg. pig-iron (in the ordinary puddle-furnace, 1200 kg. of pig would be required); and the consumption of coal was reduced from 1500 to 1200 kg.

On Danks' puddling furnaces, see J. M. Drown (*Engineering and Mining Journal*, xvi. No. 5; *Chem. Centr.* 1874, 107).

A new method of converting pig-iron into wrought iron and steel is described by F. C. Knowles (*Monit. scient.* [3], iv. 334). He endeavours to obviate the chief inconveniences of the ordinary puddling process (great loss of heat, waste of iron by burning, imperfect purification of the iron) by separating the heating from the chemical process: (1). By the production of a very basic slag containing not more than 30 per cent. silica; (2) by the use of caustic soda and pure ferric oxide, with the view of removing sulphur and phosphorus from the iron; (3) by the use of sodium nitrate or permanganate as oxidising agent. Gaseous fuel is used, consisting of carbon monoxide mixed with air heated to 500°. The carbon oxide is either obtained from the furnaces in which the iron is remelted with coke or anthracite, or it is produced by passing carbon dioxide obtained by ignition of limestone over red-hot coke; or, lastly, by the action of water-vapour on charcoal. The carbon oxide and air are mixed in such proportions as just to burn the whole of the carbon to dioxide. This carbon dioxide may be reconverted into the monoxide, and the alternation repeated till the mixture becomes too rich in nitrogen, after which the heat of the burning gases may be utilised for heating boilers, lime-kilns, &c.

The iron in the fused state is brought into the furnace, which is made of cast iron and has its walls kept cool by a stream of water. To avoid presenting too much silica to the slag, this furnace has no lining of fire-clay, but is lined internally with a kind of enamel made of ferrous or manganous oxide, emery or bauxite, and a small quantity of caustic soda: this lining is said to be very durable. Powdered ferric oxide (hematite) is introduced into the furnace, together with the melted metal, and the mixture of carbon oxide and air is introduced through the bottom of the furnace, whereby a sufficiently uniform mixture of the contents is effected. As soon as the silicon of the pig has been converted by this treatment into a slag, the latter is removed and replaced by a mixture of caustic soda and manganiferous iron ore free from silica. The pig-iron having been freed by these reagents from carbon, sulphur, and phosphorus, is run into moulds, then cooled by water, and worked under rolls, hammers, &c.

Manufacture of Wrought Iron and Steel from Pig-iron containing Phosphorus and Manganese (p. 1111).—The iron is refined in puddling furnaces, the waste heat being used for heating steam-boilers. The charge used is a mixture of manganiferous iron with white pig, made from somewhat purer ore than that which yields ordinary pig-iron, and usually contains less than 1 per cent. of phosphorus. When the iron contains not more than 5 per cent. of manganese, it is sometimes puddled alone, but it is more generally mixed with white iron containing less than 1 per cent. of phosphorus. The charges consist of 200 to 225 kilos.; for best sheet iron, 175 kilos. of spiegeleisen containing 7 per cent. of manganese and 50 kilos. of white pig, or 50 kilos. of German spiegeleisen containing 12 per cent. of manganese and 175 kilos. of white pig-iron; and for second quality, pig-iron with 5 per cent. of manganese. The action is carried on at a high temperature, and at such a rate that only four charges of 900 kilos. of pig-iron are refined in twelve hours. The loss of iron amounts to 5 per cent. The production of 1 pt. of fine-grained iron requires the consumption of 1 pt. of coal. The manganese facilitates the purification of the iron, chiefly by forming fusible slags. The strongly basic properties of the manganous oxide are said also to promote the formation of acids from the impurities in the iron.

At the Terre-Noire Works near St. Etienne in France rails are manufactured from iron containing phosphorus. A white iron (not steel) is produced by melting pig-iron with old rails,—both irons must be poor in silicon,—removing the impurities by oxidation, and reducing the oxidised iron by the use of an alloy of iron and manganese containing from 40 to 60 per cent. of the latter metal. Almost the whole of the carbon is then removed, and a product is obtained which makes excellent rails (*Chem. Centr.* 1876, 709).

On the separation of Carbon, Silicon, Sulphur, and Phosphorus, in the Refining and Puddling Furnace, and on the Bessemer Converter, see J. L. Bell (*Journal of the Iron and Steel Institute*, 1877, 390; *Dingl. pol. J.* ccxxv. 264, 357; *Chem. Soc. J.* xxxiv. 95).

3. Preparation of Malleable Iron and Steel direct from the Ore.—

The rotatory furnace invented for this purpose by Dr. U. W. Siemens, and the mode of working it, have already been described (*2nd Suppl.* 701–704). In the *Journal of the Iron and Steel Institute*, 1875, Dr. Siemens has given an account of the results obtained at the Towcester Works, where three rotatory furnaces have been erected. About 30 cwt. of ore mixed with 9 cwt. of small coal having been charged, the furnace is rotated for 2½ hours; the slag is then tapped, and the speed of rotation increased to ball up the iron. The balls formed contain about 70 per cent. of iron and 30 per cent. of cinder, but it is found that the particles of iron are pure metal, although the slag may contain 6 per cent. or more of phosphoric acid and from 1 to 3 per cent. of sulphur. The bulk of the cinder is removed by shingling, but sufficient remains to impart to the fracture a dark appearance without any sign of crystalline texture. The metal in being worked shows what may be termed 'slag-shortness.' By repiling and reheating, crystalline iron of great purity and toughness is produced.

The following table shows the composition of some of the irons produced:—

	1	2	3	4	5	6	7
Fe . .	98.30	98.73	99.45	98.97	98.909	—	99.907
Si . .	.745	.243	.643	.565	.582	—	.640
C . .	—	—	—	.235	.225	.15	.100
P . .	.08	.032	.03	.019	.02	—	.128
S . .	.065	.071	trace	.085	.106	.09	.035
Mn . .	.144	.101	trace	.126	.158	—	trace
	8	9	10	11	12	13	
Fe . .	99.128	99.728	—	99.711	99.278	99.199	
Si . .	.717	.932	—	.065	.316	.4	
C . .	trace	trace	—	.12	.12	.15	
P . .	.125	trace	.024–.172	.077	.073	.06	
S . .	.03	trace	—	.27	trace	trace	
Mn . .	.228	.34	—	trace	.213	.201	
	14	15	16	17	18		
Fe . .	—	—	—	—	—		
Si . .	.316	.165	.23	.026	.027		
C . .	trace	trace	trace	.1	.1		
P . .	.019	.046	.083	.09	.093		
S . .	trace	trace	.06	.021	—		
Mn . .	trace	trace	trace	trace	—		

1. Hammered iron.—2. Iron from Canadian ore.—3. Iron from Towcester ore.—4. The same well rolled.—5. The same badly rolled.—6. The same badly hammered, containing slag.—7. Chatterley.—8. Towcester iron, rolled.—717 Si corresponds to 1.54 per cent. of slag.—9. Iron from Indian ores. .932 Si corresponds to 2 per cent. of slag.—10. Phosphorus in Towcester iron.—11. Homogeneous iron, from Towcester iron.—12 and 13. Towcester iron, rolled.—14. Towcester iron-bloom, containing 3.17 per cent. slag.—15. Iron, fractured bloom, crystalline texture, slag 1.58 per cent.—16. Iron, fractured bloom, texture fibrous and dull, slag 2.61 per cent.—17 and 18. Iron remelted in the refinery.

Attempts to prepare malleable iron and steel by Siemens' method at Privali are described by v. Frey (*Dingl. pol. J.* cexvii. 69).

Blair's method of preparing malleable iron direct from the ore is described by P. Tunner (*ibid.* cexvi. 304; *Jahresb. f. Chem.* 1875, 1017).

4. *Fibrous Iron*.—H. Le Chatelier observes (*Compt. rend.* lxxxii. 1057) that when fibrous iron is heated to dull redness in a stream of chlorine, there remains, after the volatilisation of the iron chloride, an extremely thin, greenish-white network composed of threads of slag, and to the enclosure of these threads in the mass of iron he attributes its fibrous structure. This network of threads appears to be formed when the slag is difficult of fusion and the iron is puddled at a comparatively low temperature. Fibrous iron smelted with charcoal from the Jura was found to contain 0.7 per cent. of this slag; fibrous charcoal-iron from Belgium yielded 1.3 per cent.

5. *Cause of Brittleness in Wrought Iron*.—F. Kick (*Dingl. pol. J.* cxxiii. 358) observes that the molecular change in wrought iron which results in brittleness is brought about, not only by frequent agitation, but also by sudden cooling from a high temperature. Boiler plate 10 mm. thick heated not quite to redness, and then quickly cooled in water, exhibited a crystalline layer 1 mm. thick on each side of the nucleus, which had remained fibrous. Kick is of opinion that this change of structure may lead to the bursting of steam-boilers.

On Homogeneous Iron and the degree of Homogeneity to be expected in Iron produced by various systems of Puddling and subsequent Working, see *Engineer*, May 11, 1877, and *Chem. Soc. J.* xxxiv. 253-257; also *Dingl. pol. J.* cxxvi. 394; *Chem. Soc. J.* xxxiv. 257.

6. *Burnt Iron* (2nd Suppl. 700).—According to H. Caron (*Compt. rend.* lxxvii. 836) burnt iron may be regenerated, that is to say, restored to the state of malleability, by plunging it, while red-hot, into a saturated solution of common salt, till its temperature is reduced to about 110°.

7. *Soft Iron*.—J. A. Cabell (*Chem. News*, xxx. 142) has analysed iron found in crystalline granules on the wall of a welding furnace, in which Heaton steel had been heated for forging. This iron was soft, easy to file and saw, did not become hard by sudden cooling, and showed indeed all the properties of bar iron. Sp. gr. 7.86. Its composition was remarkable, as shown by the following analysis

C	Si	S	P	Fe
1.121	0.024	0.037	0.436	98.382 = 100.

8. *Spongy Iron* (G. Lunge, *Dingl. pol. J.* cexix. 325).—The preparation of this kind of iron, which is extensively used for the reduction of cement-copper, requires the uniform heating of an extended porous mass. This is effected by heating the ore and reducing agents in a reverberatory furnace having a very wide horizontal sole. Vertical partitions divide the over-arched heating space into three parts, each provided with two working doors in the side walls. These divisions are filled through doors in the arched roof, on which the materials have been previously warmed, and they are emptied by pipes passing downwards from the working doors in the sole; these pipes may be connected with conically widening collecting vessels which can be tightly closed. The grate, situated 1.422 m. below the fire-bridge, admits of a thick layer of fuel and thereby ensures a constant reducing flame. The fire-gases, after leaving the furnace, pass over the sole, composed of chamotte tiles, and finally arrive at the reducing furnace. The furnace, which is raised to a bright red heat, admits of the introduction in each division of 20 ctr. of dry 'purple ore' (impure ferric oxide from the copper extraction) mixed with 6 ctr. of comminuted and sifted coal to reduce it. The process is completed in nine to twelve hours in the first division, in eighteen hours in the second, in twenty-four hours in the third division, and requires in these intervals repeated working of the materials with closed furnace doors. The spongy iron, after cooling in the collecting boxes, is ground, sifted, and used for the precipitation of copper.

9. *Bronzing of Iron*.—For this purpose Ph. Hep recommends, in place of a film of ferric oxide, which is difficult to produce, the formation of a film of ferroso-ferric oxide. This is produced by smearing the surface of the iron with linseed oil, and then heating it, or if a strong heat is inadmissible, dipping the uniformly oxidised article into water at 100°. Still more quickly is the bronzing produced in an acid bath of ferric chloride. The ferroso-ferric oxide which forms after a while attaches itself closely to the surface on immersing the object in hot water, and after drying may be rubbed in with linseed oil or wax. It is true that objects bronzed with ferroso-ferric oxide are liable to rust after some time, but the bronze-surface does not peel off, and the rust is easily brushed off.

Iron surfaces may also be protected by forming cuprous sulphide upon them. For this purpose the objects, after being cleaned, are dipped in solution of cupric sulphate, and as soon as a thin film of copper is formed on them, they are rinsed with water, and treated with a slightly acid solution of sodium thiosulphate, whereby a black deposit of cuprous sulphide is formed. The surface, after drying with blotting paper, and treatment with the burnishing stick, exhibits a steel-blue shimmer, and withstands satisfactorily the action of atmospheric agents.

10. *Coating of Iron with other Metals*.—(1). With Copper. The following methods are described by A. Gaudoin (*Dingl. pol. J.* ccciii. 50). a. The required quantity of copper is fused in a crucible; the metal bath is covered with a flux of cryolite and phosphoric acid; and the iron, after being heated to the temperature of the bath, is dipped into it.—b. A mixture of 1 pt. dry chloride or fluoride of copper, and 5 or 6 pts. of cryolite, to which 'a certain quantity' of barium chloride may be added, is fused, and the iron, after being cleansed with acid, is dipped into this bath. The deposition of the copper may be accelerated by a voltaic current.—c. For the coppering of iron in the wet way, a strongly acid solution is required. An excellent bath for the purpose is made by dissolving cupric oxalate and a large excess of potassium bi- or quadroxalate in a ten to fifteenfold quantity of water. In this case also the aid of the current is advantageous.

On the Coppering of Cast Iron Rollers for Calico-printing, by Electrolytic deposition, see G. Schäffer (*Bull. Soc. industr. de Mulhouse*, xlv. 120; *Jahresb. f. Chem.* 1874, 1093; *Chem. Soc. J.* xxviii. 1967).

(2). With Zinc. The iron is first cleansed with dilute sulphuric acid, and immersed for a time in water mixed with milk of lime. It is then dipped, first into a solution of zinc chloride (prepared by saturating common hydrochloric acid with zinc) containing a quantity of sal-ammoniac equal to $\frac{1}{10}$ per cent. of the weight of the zinc chloride. In this solution the iron becomes covered with a thin coating of zinc, the thickness of which may be increased by immersing the dried iron in fused zinc till it has acquired the temperature of the bath (*Dingl. pol. J.* ccvii. 340). On the 'galvanisation' of iron, see also F. A. Thum (*ibid.* ccxvi. 339).

(3). With Nickel. The bath used consists of a 5 to 10 per cent. solution of zinc sulphate containing a quantity of nickel sulphate sufficient to give it a bright green colour (Böhm, *Ber.* 1876; *Jahresb. f. Chem.* 1876, 1103). According to Hess (*Dingl. pol. J.* ccxvii. 256) the nickel bath used by Plazanet consists of 87.5 grams nickel sulphate, 20 ammonium sulphate, 17.5 citric acid, and 2 litres of water. According to Boden (*ibid.*), a nickel bath much used in France is prepared by dissolving 4 pts. nickel nitrate in 4 pts. aqueous ammonia, and 150 pts. water holding in solution 50 pts. of acid sodium sulphite. With the aid of a very feeble current the deposition is completed in a few minutes. There is no necessity for interrupting the process in order to clean the surface and thereby ensure the desired thickness of the deposit; the nickelled objects merely require to be dried in sawdust.

(4). With Tin. Iron tacks may be tinned by triturating zinc chloride with a considerable quantity of oil; heating the mixture in a swinging pot; then adding the tacks, together with the requisite quantity of tin; after a few seconds the tinned tacks are withdrawn by means of a wire net and thrown into water (*J. Wiley, Berl. Ber.* vii. 1465).

(5). With Gold and Silver. To obtain iron capable of being directly silvered or gilt, Delatol (*Dingl.* ccxv. 471) adds to 1,000 pts. of cast iron, 12 pts. nickel, and 0.5 pt. manganese. Objects made of this alloy require merely to be cleansed with milk of lime, and may then be plunged into the following baths.

<i>Gold-bath.</i>		<i>Silver-bath.</i>	
Water	100 pounds.	Water	100 pounds.
Sodium Bicarbonate	4½ "	Sodium Bicarbonate	2 "
Sodium Pyrophosphate	1½ "	Silver Chloride or Nitrate	2 oz. "
Auric Chloride	¼ oz. "	Potassium Cyanide	6 "
Sodium Cyanide	1 "	Hydrocyanic Acid	10 drops.
Hydrocyanic Acid	2 drops.		

11. *Etching of Iron and Steel.*—The action of acids on various kinds of iron and steel produces markings which give an insight into the structure of the metal, its composition, and the manner in which it has been worked. A convenient etching fluid is composed of 1 pt. hydrochloric acid, 1 pt. water, and a trace of antimonie chloride (one drop of a strong solution of the latter to a litre of the dilute acid.) The surface to be etched, having been previously rendered even by filing or grinding, is surrounded with a ridge of wax about ¼-inch high; the acid is poured into the space thus marked off; and the progress of the etching is observed every half-hour, the acid being renewed if necessary. When the etching is complete, the surface is washed, first with alkaline and then with pure water, and protected from rusting by a coating of Dammar varnish. The addition of antimony chloride to the etching liquid serves also to prevent too rapid rusting.

Soft fibrous iron thus treated is etched so uniformly that the surface remains light-coloured and with a faint lustre, but little carbon separating out; imperfect spots or ash-cavities however are brought to light. *Fine-grained iron* exhibits a similar aspect, the etched surface being generally more uniform, but darker in colour. *Coarse-grained and cold-short iron* is strongly attacked by the acid; the etched surface under the acid becomes black in ten minutes; and after thirty minutes a black deposit may be washed off it, the metal itself however remaining black and being marked with numerous small holes. *Malleable cast-iron* is very strongly and uniformly etched. *Puddle-steel, cement-steel, and Bessemer steel* yield uniform light-grey etch-surfaces, in which the lines of separation of the layers and imperfect spots show themselves, the finest capillary fissures being brought to light by the etching. *Grey pig-iron* yields a dark-grey uniform etching. *Soft iron* distinctly shows the white constituents as light-grey markings on the dark ground formed by the grey pig. The application of this etching process to finished goods shows the kind of metal of which they are made and the manner in which it has been worked. The mode of packing in the forge may in like manner be recognised in the finished pieces (F. Kick, *Dingl. pol. J.* ccxii. 40).

III. *Steel. Preparation from Cast Iron. Bessemer Process.*—Cast iron for this purpose should be rich in silicon, but as free as possible from sulphur and phosphorus. Only a few ores yield pig-iron of this description; the best is red hematite, then come brown hematite, magnetic iron ore, and lastly clay iron ore, in so far as this last can be used for making Bessemer steel (W. Baker, *Chem. News*, xxvii. 25).

P. Tunner (*Dingl. pol. J.* ccxv. 507) observes that a large proportion of silicon in pig-iron certainly facilitates the Bessemer process by raising the temperature of the furnace; but that, on the other hand, it is scarcely possible to obtain steel free from silicon by the use of pig-iron containing that element in large proportion. If the product is to be used as unhardened steel, the presence of silicon is not objectionable, but it greatly interferes with the hardening of steel. Tools and articles of similar description should therefore never be made of Bessemer steel prepared from siliciferous iron; steel for such purposes is best prepared by casting.

Rochussen a. Daelen prepare steel from pig-iron by lining the Bessemer converter with ferric oxide (pulverised ore), which supplies at least half the oxygen required to burn out the carbon; consequently the quantity of air required to be blown into the converter is less than in the original process, and the quantity of steel obtained is increased by the reduction of iron from the furnace lining. The temperature of the furnace is at least as high as when no ferric oxide is used, and is indeed increased by the combustion of the carbon oxide resulting from the mutual action of the ferric oxide and the carbon of the iron. As the carbon oxide is not formed till the metal bath has become strongly heated by the combustion of the silicon, a larger quantity of air is required in the latter stages of the process than at the beginning. To ensure this, the tuyere-holes at the bottom of the converter are closed at first by the furnace lining, and it is only when this lining melts that the blast has full play (*Engineer* April 1873, p. 249; *Dingl. pol. J.* ccix. 416).

H. Schwarz observes that, in working the Bessemer process, it sometimes happens that the usual appearances indicating the end of the operation present themselves before the oxidation of the carbon is really complete. This happens most frequently when the charge becomes too hot, and Schwarz considers it probable that under these circumstances the temperature of dissociation of carbon dioxide is reached, so that the oxygen of the air passes through the molten iron without combining with the carbon.

Use of Ferromanganese and Spiegeleisen in the Bessemer process (F. Gautier, *Dingl. pol. J.* cxxii. 48).—The ferrosiferrous oxide formed in the Bessemer process when no manganese is employed, passes into the steel and renders it red-short, whereas manganese, if present, reduces the ferrosiferrous to ferrous oxide which, together with the manganous oxide formed at the same time, readily passes into the slag. A certain quantity of manganese is nevertheless found in the steel produced, and it is not yet ascertained how far the improved quality of the product is due to its presence. In the Bessemer and Siemens-Martin processes, from 1 to 10 per cent. manganese is added to the steel in the form of Spiegeleisen. The use of this alloy is however attended with an increase in the proportion of carbon in the product, and to avoid this, manganese alloys containing 75 per cent. manganese, prepared at the Terre Noire works, have lately come into use. Gautier is of opinion that the addition of 1 per cent. manganese in this form to the molten mass is sufficient for the preparation of the softest steel: for, as was first observed by Bessemer, the manganese removes from the steel, not only ferrosiferrous oxide, but likewise the greater part of the carbon. A specimen of steel prepared with ferromanganese showed a somewhat narrower range of elasticity and a somewhat smaller coefficient of tenacity than steel obtained with spiegeleisen; on the other hand its extensibility was more than three times as great as that of spiegeleisen steel. Now Mallet has shown that the constructive value of steel for parts of machinery, plates, &c., is measured by the product of the coefficient of tenacity into the final expansion: hence it follows that, for the uses just mentioned, ferromanganese steel is decidedly preferable to spiegeleisen steel, notwithstanding the greater tenacity of the latter. The product just mentioned is for hard steel, 305; for soft ferromanganese steel, 700; for ordinary iron, 105. It is recommended to add the ferromanganese red-hot to the mass in the converter, since such a mass added in the cold state might give rise to dangerous spitting.

The association of carbon with silicon greatly interferes with the preparation of soft steel, whereas steel not containing carbon forges readily even if it contains 7·5 per cent. silicon. Sulphur, if present in the raw material even to the amount of 1 per cent., may be removed almost completely, during the smelting in the blast furnace, by a copious addition of lime or manganese.

2. Phosphorised Steel.—The proportion of phosphorus in steel containing 0·5 per cent. carbon must not exceed 0·05 per cent., otherwise the steel will not roll well. The removal of the carbon from such steel by the use of ferromanganese is especially desirable, since it has been found that steel containing as much as 0·4 per cent. phosphorus may be rendered soft and tenacious, provided that the proportion of carbon in it is reduced to a mere trace. Phosphorised steel becomes softer by rolling, its granular texture changing at the same time into fibrous. The presence of a somewhat considerable proportion of manganese, up to 1 per cent., in phosphorised steel increases its power of resisting shocks. A so-called manganese-steel, very poor in carbon, may be prepared by the Bessemer or Siemens-Martin process, if 1·5 per cent. manganese in the form of ferromanganese be added to 60–75 per cent. of the fused metal; the product is a steel containing 1 per cent. manganese, and at most 0·5 per cent. carbon. Such steel is very flexible, and exhibits great resistance to shocks.

A. Greiner (*Rev. scient.* 1874, xxxv. 623; *Dingl. pol. J.* ccxvii. 33) describes the manufacture of phosphorised steel at the Königin-Marien Works at Kainsdorf near Zwickau, and at the Max Works near Schwandorf in Bavaria. The pig-iron used at Zwickau contains on the average 2·50 per cent. silicon, 0·04 sulphur, 0·10 to 0·12 phosphorus, 2·6 to 4 manganese, and 3·5 carbon; that of the Max Works contains 0·10 per cent. phosphorus (minimum), and 4 per cent. manganese. These pig-irons, when remelted in the cupola, take up an additional quantity of phosphorus from the ash of the coke, which at the Max Works sometimes contains from 0·33 to 0·4 per cent. phosphorus. The reaction between the blast and the metal in the converter is very violent, and the converter is therefore made higher than usual, in order to prevent the slag from being forcibly thrown out. The steel decarburised by the blast towards the end of the refining operation contains so much manganese, that the addition of spiegeleisen may be dispensed with, and the metal run off directly at the moment of completion.

The spectroscopic recognition of the completion of the process is more difficult in

the case of manganese pig than in the ordinary operation of refining, partly from the intense brightness of the flame produced by the oxidation of the manganese, and partly from the thick smoke of brown oxides arising from the liquid mass. Towards the end of the operation, however, the black lines towards the blue end of the spectrum disappear, and those in the green become fainter; then the latter disappear, while those in the yellow become faint, and so on. When all these absorption-bands have vanished, and the spectrum has again become continuous, the decarburisation is known to be nearly completed. The blast may then be continued a minute or two longer; a sample of the contents of the converter—metal and slag—taken out on the end of an iron rod; the colour of the slag is examined, and the hardness of the metallic globules tested by hammering. If the slag is black on the outside, the steel is very soft; a brown colour of the slag also indicates soft steel; orange, half-hard; and dark-yellow, hard steel. A globule of soft steel may be hammered out to a plate without any cracks on the edges; but the harder the steel, the deeper and more numerous will be the cracks.

At the Marien Works, two converters holding 5 tons each yield in 24 hours and 14 tappings, 63 tons of manganese steel, about 10 per cent. of the metal being lost by burning. The steel contains from 0·4 to 0·7 per cent. silicon, 0·06 sulphur, 0·10 to 0·15 phosphorus, 0·4 to 0·7 manganese, and about 0·15 carbon. Steel containing more than 0·20 per cent. phosphorus is brittle.

The chief use of the phosphorised steel above described is for the manufacture of rails. For this purpose the ingots are rolled to covering plates of 40 to 50 mm. thickness, and of the breadth of the packet of rails, and under these covers the rails of coarse-grained phosphorised iron are placed, whilst above, a flat bar of fibrous iron is brought to form the foot of the iron rail. The coarse-grained iron serves to combine the steel head with its basis of fibrous iron. A packet so composed endures a welding heat very well, and in rolling exhibits a very close resemblance to ordinary railway iron. A 'mixed' rail is thus obtained, which when carefully made is very durable.

Phosphorus makes steel cold-short, and diminishes its elasticity as regards drawing or bending strain. Good steel, containing 0·15 to 0·60 per cent. carbon, may be elongated without breaking, to the extent of 9 to 10 per cent. of its original length, whereas steel containing 0·25 to 0·38 per cent. phosphorus breaks when stretched only to the amount of 3 to 4 per cent. A steel prepared from pig-iron containing 0·69 per cent. phosphorus was found to be as brittle as glass. These defects are remedied to a certain extent by the presence of manganese, this metal removing the ferric oxide present in the decarburised bath, thereby rendering the metal capable of welding, and restoring its extensibility.

3. Cementation Steel.—The changes which iron undergoes in its conversion into steel by cementation have been studied by M. Boussingault (*Compt. rend.* lxxviii. 1458). The iron was weighed before and after cementation. Iron smelted from spathic iron ore and hematite in the Ria Works (East Pyrenees) was subjected to cementation in two pieces. One piece weighed 4949·54 grams before and 4994·20 grams after cementation, it had therefore gained 44·65 grams. The corresponding numbers in the second piece were 5124, 5199·6, and 75·6. The analysis of the metal gave—

	Before cementation	After cementation	
		No. 1.	No. 2.
Iron	99·100	98·200	97·650
Combined carbon	0·118	0·995	1·512
Silicon	0·105	0·107	0·120
Sulphur	0·012	0·006	0·005
Phosphorus	0·100	0·125	0·130
Manganese	0·222	0·220	0·218
Undetermined	0·343	0·347	0·365
	100·000	100·000	100·000

In both cases, the increase of weight exceeded the weight of the carbon fixed, and the silicon, phosphorus, and undetermined matters which were acquired, weighed more than the iron and sulphur lost.

A second experiment was made on a bar of Swedish iron. After cementation, the blistered surface was covered with graphite. The metal itself was of silvery whiteness.

The results of the analysis were as follows :

	Weight of the bar	Iron	Carbon	Silicon	Sulphur	Phos- phorus	Man- ganese	Unde- ter- mined
Before cementation	2000.45	1989.45	6.00	0.32	0.30	1.14	1.80	1.44
After cementation	2026.22	1989.14	32.01	0.61	0.10	1.32	1.42	1.62
Differences . .	+ 25.77	- 0.31	+ 26.01	+ 0.29	- 0.20	+ 0.18	- 0.38	+ 0.18

* The increase of the weight of the bar was slightly less than the weight of the carbon fixed.

A slight loss of iron always occurs in cementation: this was found to be the case even in an experiment with pure iron. Boussingault attributes this loss to the volatilisation of ferric chloride formed from the metallic chlorides which are always present in the ash of charcoal; moreover, the powdered charcoal used for the cementation always takes up a small quantity of iron. The combination of the iron with carbon is always attended with elimination of sulphur, which also goes on to a greater extent in the refining of the crude steel, *e.g.* by remelting. The best steel contains nothing but iron and carbon; all other constituents of wrought iron must be removed, or should remain in the steel in inappreciable quantities only.

H. St. Claire Deville (*Compt. rend.* lxxviii. 1464) is of opinion that the blisters on the surface of crude cementation steel are due to hydrogen which is absorbed during the cementation and afterwards given up. Berthelot (*ibid.* 1465) considers that iron, like palladium, is capable at a dull red heat of forming with hydrogen a chemical compound, which is decomposed at a higher temperature. The deposition of graphite on the surface of the crude steel is attributed by Berthelot to the decomposition of a compound of iron and carbon, which is perhaps formed by direct combination of its elements, or may be produced by the agency of hydrocarbons.

4. *Cast Steel*.—On the preparation of cast steel by the Bessemer and Martin processes, see Noblot (*Revue universelle des Mines*, xxxiii. 33; *Dingl. pol. J.* cxx. 197; *Jahresb. f. Chem.* 1873, 1004).

On the use of Alloys of Silicon and Manganese in the preparation of Cast Steel, see S. Kern (*Chem. News*. xxxv. 226; *Chem. Soc. J.* xxxii. 522).

5. Mushet's 'Special Steel.' This steel contains, according to Heeren (*Dingl. civ.* 477), 8.3 per cent. tungsten and 1.73 manganese; according to Gintl a. Janowsky (*ibid.* cxx. 271), 8.813 to 8.741 tungsten and 2.575 to 2.480 manganese; according to Gruner (*ibid.* cxvii. 316), 7.98 per cent. tungsten, together with 1.40 carbon and 0.24 silicon: he supposes that Mushet obtained it by fusing pure cementation steel with metallic tungsten. Heeren and Gruner find that Mushet's steel in its original state has the hardness of good glass-hard steel; when subjected to the process by which ordinary steel is hardened, it becomes softer, and cracks in all directions. It may be forged at a red heat, and must be brought into the required shape by forging, as it cannot afterwards be filed. It also possesses a degree of toughness which renders it well adapted for the manufacture of cutting instruments. According to Kick, on the other hand (*ibid.* cxx. 488), this steel is very difficult to work, and tools made of it soon lose their edge. According to Kellerbauer (*ibid.* cxvii. 488), the only advantage that Mushet's steel possesses over other kinds is that it does not require hardening; on the other hand, its utility is greatly limited by the difficulty of working it.

Alloys resembling steel may be prepared by fusing iron with nickel and tungsten in the following proportions:

Soft Iron	Tungsten	Nickel
93	6.5	0.5
95	4.5	0.5
97	2.5	0.5

As a flux may be used a fused mixture of 50 parts boric oxide, 32 sand, and 32 calcium carbonate (H. Levallois, *Dingl.* cxx. 235).

6. *Hardening of Steel*.—H. Caron (*Compt. rend.* lxxvii. 836) recommends for this purpose the use of water at about 55° C. Steel plunged into water at this temperature does not crack, as it often does when hardened with cold water.

A. Jarolimek (*Dingl. pol. J.* cxxxi. 436) observes that thin steel wires are completely hardened by immersion, not only in boiling water, but likewise in boiling oil, and in melted lead or tin, and even in melted zinc, provided that they are dipped in the zinc-bath for a short time only, whereas they lose their hardness by prolonged immersion therein. Hence Jarolimek concludes that the hardening of steel depends

on sudden cooling below 500°, whereas tempering or softening is completed within lower limits of temperature. The fitness of a liquid for hardening steel depends upon its heat-conducting power and heat capacity, water being, especially for the last reason, preferable to all other liquids, although the film of vapour formed at the same time round the glowing steel tends by its low conductivity to retard the cooling of the steel. This inconvenience may, however, be obviated by immersing the red-hot steel in a stream of hot water spray, the water being then rapidly converted into vapour, and the vapour at the same time quickly removed. Steel thus treated acquires the hardness of glass. The *tempering* of steel is also easily effected by this process, either by diminishing the force of the spray or by removing the steel into the more diffused part of it.

To protect steel objects from oxidation during the hardening process, Ph. Rust (*Dingl. cexxi.* 284) coats them with a thin paste of 2 parts charcoal, 1 part yellow prussiate and glue, after which they may be heated to redness in a charcoal fire and hardened.

On the Hardening of Steel, see further F. Dietlen (*Dingl. cexxi.* 518; *Jahresb. f. Chem.* 1876, p. 1069); also Garman a. Siegfried (*Dingl. ccx.* 472; *Jahresb.* 1873, 1005).

On the Influence of Heat on the Hardening of Steel, see Metcalf (*Dingl. cexxix.* 92; *Chem. Soc. J.* xxxiv. 1019).

For the regeneration of burnt steel, Kolicke (*Dingl. ccviii.* 463) recommends a mixture of 12 parts by weight of tartaric acid, 60 cod-liver oil, 4 charcoal-powder, 16 bone-black, 20 beef-suet, 10 yellow prussiate, and 6 burnt hart's horn. The red-hot steel is dipped into the pasty mass and then quenched in water.

7. Relation between the Physical Properties of Steel and its amount of Carbon.—An examination by W. Langly (*Amer. Chemist*, vii. 175) of twelve samples of steel which had previously been remelted, showed that with varying proportions of carbon, from $\frac{1}{16}$ per cent. upwards, the appearance of the fracture exhibited differences easily recognisable by a practised eye. The density was also found to diminish proportionally to the increase in the amount of carbon. Steel which has been very strongly heated and quickly cooled—so-called *burnt steel*—is well known to exhibit a very coarse granular texture on the fracture-surface. The specific gravity of the steel is also diminished by this process, the decrease being greater in proportion as the hardened specimen has been more strongly heated.

The decrease of specific gravity with increasing amount of carbon has also been observed in Bessemer steel by Koppermayer (*Dingl. pol. J.* cexi. 22), as shown in the following table:—

Percentage of carbon	Specific gravity of the steel at 13°
0.14	7.9219
0.19	7.8784
0.30	7.8754
0.46	7.8711
0.55	7.8632
0.57	7.8569
0.66	7.8530
0.80	7.8434
0.87	7.8378
0.96	7.8291

On the Influence of an Electric Current on the Electric Conductivity of Iron and Steel, see ELECTRICITY (p. 718).

On the Magnetisability of Iron and Steel, see MAGNETISM.

On the Occlusion of Gases by Steel, see p. 1113.

According to S. Kern (*Chem. News*, xxvi. 19; *Chem. Soc. J.* xxxii. 815), the steel in the metallic bath of the Bessemer converter contains oxygen in the occluded state, and perhaps in the form of a definite chemical compound analogous to hydrogen-palladium. Five specimens analysed gave 0.054, 0.037, 0.025, 0.040, and 0.031 per cent. oxygen.

Classification and Nomenclature of Iron and Steel.—An International Commission formed in connection with the Philadelphia Exhibition in 1876, recommended the adoption of the following terms (English, German, French, Swedish):—

(1.) Weld-iron (*Schweiss-eisen, fer soudé, wäljern*) for all malleable compounds of iron with the ordinary ingredients, which have been prepared from softened masses

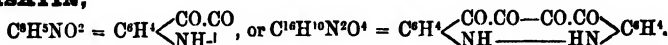
or faggots, or in any form other than the liquid state, and cannot be hardened or tempered, and are similar to the substance commonly called wrought-iron.

(2.) Weld-steel (*Schweiss-stahl*, *acier soudé*, *wällstål*), for compounds of the previously described quality which from any cause are capable of being hardened and tempered, and are therefore similar to the product hitherto called 'puddled steel.'

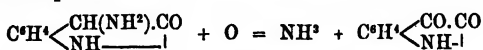
(3.) Ingot-iron (*Fluss-eisen*, *fer fondu*, *götjern*), for all compounds of iron with the ordinary ingredients which have been cast in the liquid state to malleable masses and cannot be appreciably hardened when placed in water whilst red-hot.

(4.) Ingot-steel (*Fluss-stahl*, *acier fondu*, *götslål*), for compounds of the last described quality which from any cause are capable of being tempered (*Dingl. pol. J.* cxxiii. 325; *Chem. Soc. J.* xxii. 239). See also Greiner (*Chem. Centr.* 1873, p. 759; *Chem. Soc. J.* xxvii. 830).

ISATIN,



The formation of this compound by oxidation of amidoxindole (p. 1087) may be represented by the equation—



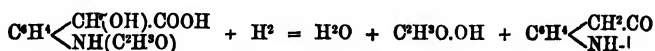
Now oxindole, $\text{C}^6\text{H}^4 \left\langle \begin{array}{c} \text{CH}^2.\text{CO} \\ \text{NH} \end{array} \right\rangle$, is identical with the anhydride of orthamidophenylacetic acid, and isatin is converted into indigo-blue by heating it with a mixture of PCl^3 and PCl^5 , and subjecting the product to the action of reducing agents: hence this series of reactions affords the means of preparing indigo-blue from a compound belonging to the coal-tar group (p. 1086).

Acetyl-derivatives of Isatin (W. Suida, *Berl. Ber.* xi. 584). *Acetyl-isatin*,

$\text{C}^6\text{H}^4 \left\langle \begin{array}{c} \text{CO} \text{—————} \text{CO} \\ \text{N}(\text{C}^2\text{H}^3\text{O}) \end{array} \right\rangle$, prepared by heating isatin with twice its weight of acetic anhydride for three or four hours, crystallises in yellow prismatic needles which melt at 141° . It dissolves easily in benzene and in alcohol, and is resolved into isatin and acetic acid by boiling with water, or more readily with hydrochloric acid.

Acetylisisatic Acid, $\text{C}^6\text{H}^4\text{NO}^4 = \text{C}^6\text{H}^4 \left\langle \begin{array}{c} \text{CO.CO.OH} \\ \text{NH}(\text{C}^2\text{H}^3\text{O}) \end{array} \right\rangle$, obtained by dissolving acetyl-isatin in dilute potash-ley and precipitating with dilute sulphuric acid, is a white crystalline substance, melting at 160° , sparingly soluble in cold water, more easily in alcohol, ether, and benzene; converted into isatin by boiling with hydrochloric acid. It dissolves in soda-ley, but the solution quickly undergoes alteration. The lead and silver salts are white precipitates.

Acetyl-hydrindic Acid, or *Acetyl-dioxindole*, $\text{C}^6\text{H}^4 \left\langle \begin{array}{c} \text{CH}(\text{OH}).\text{CO.OH} \\ \text{NH}(\text{C}^2\text{H}^3\text{O}) \end{array} \right\rangle$, obtained by the action of sodium-amalgam on a solution of acetylisisatic acid in acetic acid, forms colourless needle-shaped crystals, melting at 142° , easily soluble in water, alcohol, chloroform, and glacial acetic acid; insoluble in light petroleum. It does not yield isatin when boiled with hydrochloric acid. By reducing agents (hydriodic acid or sodium-amalgam) it is resolved into acetic acid and oxindole—



Amido-derivatives of Isatin (E. v. Sommaruga, *Liebig's Annalen*, cxc. 367; *Berl. Ber.* xi. 1082). When an alcoholic solution of isatin saturated with dry ammonia-gas is heated to 100° in sealed tubes for 24 hours, two crystalline bodies are formed, one slightly soluble, the other easily soluble in water and in alcohol, together with a resinous substance and a very small quantity of a purplish-red colouring matter.

1. *Amido-isatin*, $\text{C}^6\text{H}^4\text{N}^2\text{O} = \text{C}^6\text{H}^4(\text{NH}^2)\text{NO}$, or *Diamido-diisatin*, $\text{C}^{16}\text{H}^{12}\text{N}^4\text{O}^2 = \text{C}^{16}\text{H}^8(\text{NH}^2)^2\text{N}^2\text{O}^2$, the less soluble of the two crystalline bodies, is produced in the manner shown by the equation—

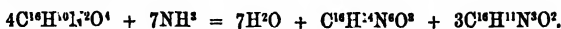


It forms pale yellow crystals, sparingly soluble in alcohol and in water, melts with decomposition at 111° , and forms salts with acids. The *hydrochloride*, $\text{C}^{16}\text{H}^{12}\text{N}^4\text{O}^2.\text{HCl}$, and the *nitrate*, $\text{C}^{16}\text{H}^{12}\text{N}^4\text{O}^2.\text{NO}^3\text{H}$, are yellow crystalline powders slightly soluble in

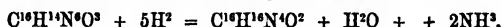
water. The *sulphate*, $C^{16}H^{12}N^4O^2 \cdot SO^4H^2$, crystallises in light yellow needles; the *chromate*, $C^{16}H^{12}N^4O^2 \cdot CrO^4H^2$, is an orange-coloured powder.

Diamido-diisatin is converted by sodium-amalgam into the compound $C^{16}H^{12}N^4O^2$, which is insoluble in water, but crystallises from alcohol in small colourless needles. Its sodium-derivative, $C^{16}H^{12}NaN^3O^2$, crystallises in long colourless needles, very soluble in water; the potassium-derivative, $C^{16}H^{12}KN^3O^2$, in broad needles, having a silky lustre.

Oxydiimido-diamido-diisatin, $C^{16}H^{11}N^6O^2 = C^{16}H^8(NH)^2(NH^2)^2N^2O^2$, the easily soluble crystalline body, and *Deoxyimido-diisatin*, $C^{16}H^{11}N^3O^2 = C^{16}H^{10}(NH)N^2O^2$, the resinous compound above mentioned, are formed simultaneously in the manner shown by the following equation:



Oxydiimido-diamido-diisatin forms large colourless needle-shaped crystals, which melt between 295° and 300° , and dissolve readily in acids. When treated with potassium nitrate and sulphuric acid, it yields a nitroso-product, which is decomposed by water, and has not been obtained pure. By sodium-amalgam, the oxydiimido-compound is reduced in the manner shown by the equation—



The product, which is possibly the amide of hydrindic acid or dioxindole, $C^8H^8(NH^2)O^2$ (or the diamide of dihydrindic acid), is converted by oxidation with chromic acid mixture into an acid, $C^{16}H^{12}N^4O^4$, which may be called *diimido-hydrincarbonic acid*: $C^{16}H^{16}N^4O^2 + O^2 = 2H^2O + C^{16}H^{12}N^4O^4$.

Deoxy-imido-diisatin, $C^{16}H^{11}N^3O^2$, when purified by solution in potash, and reprecipitation by an acid, forms a yellowish powder resembling tannin. It melts, with decomposition, at 209° – 210° , and dissolves in alcohol and in water. Sodium-amalgam converts it into an amorphous isomeride of monamidodihydro-diisatin—



The same product is formed by the action of water or strong potash-ley under pressure on deoxy-imido-diisatin.

The existence of the compounds above described is regarded by v. Sommaruga as showing that the molecule of isatin—and therefore also that of indigo-blue—contains 16 atoms of carbon. This conclusion is in accordance with a recent determination, by Sommaruga, of the vapour-density of indigo-blue which was found, as the mean of nine experiments, to be 9.45, the formula $C^{16}H^{10}N^2O^2$ requiring 9.06. Isatin decomposes when vapourised, so that its vapour-density cannot be directly determined.

ISENITE. Sandberger described under the name of *Nosean-andesite* a volcanic rock which occurs at several localities in Nassau, especially on the Sengelberg near Sala in the Wisterwald, also on the Kriegershecke near Wöflerlingen, and near Maxhayn (*Jahrb. f. Min.* 1874, 319). This same rock has been subjected to a very careful mineralogical, microscopical, and chemical investigation by G. A. Bertels (*ibid.* 873), who calls it *Isenite*, from the name of a small river in Nassau, the Eis (formerly *Isen*). The main results of this investigation are as follows:—

Amongst the macroscopically distinguishable constituents of the rock, the felspars, which are mostly unaltered, exhibit under a magnifier, distinct twin-marking. Hornblende appears in fine twin-crystals of known form, often however converted on the edges into a radiate mineral. Octohedrons of magnetic iron-ore and hexagonal titaniferous iron occur, as well as rhombic crystals of a red-brown mineral, recognised by Bertels as allied to fayalite. Lastly, needles of apatite are also found. The zeolitic mineral in the cavities is stilbite.

Microscopic examination showed, in the first place, a light-coloured ground-mass consisting of triclinic felspar, in which were imbedded tablets of ferruginous mica, granules of magnetic iron ore, and especially well-developed noseans regularly disseminated through the rock. Distorted hexagons of nephelin occur as subordinate constituents. The large crystals of felspar already mentioned frequently enclose granules of magnetic iron, laminae of iron-glance, glass-cells, vapour-pores, fine needles of apatite, and more rarely small noseans. The large hornblendes are often quite filled with granules of magnetic iron ore; needles of apatite and fayalite are also found in them, and even comparatively large crystals of fayalite, apatite, and felspar.

The powdered rock cautiously warmed with hydrochloric acid yields a distinct jelly. A chemical analysis of the entire rock, as well of the soluble part (36.74 per cent.) and of the insoluble part (64.26 per cent.), gave the following results. Sp. gr. = 2.78:

	Total analysis	Soluble	Insoluble
Silica	48.02	8.20	39.82
Alumina	16.92	2.41	14.51
Ferric oxide	11.63	10.74	0.89
Ferrous oxide	4.70	2.83	1.87
Manganous oxide	2.44	0.50	1.94
Magnesia	1.45	1.15	0.30
Lime	8.58	3.64	4.94
Soda	2.36	2.36	0.93
Water	1.78	1.78	—
Titanic acid	0.15	—	0.15
Phosphoric acid	1.55	1.55	—
Sulphuric acid	0.56	0.56	—
Chlorine	0.53	0.53	—
	<hr/> 100.67	<hr/> 36.25	<hr/> 65.35

A remarkable circumstance is the absence of potash, which could not be detected even spectroscopically.

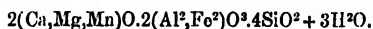
Bertels has also analysed some of the separable constituents of the rock, viz., the felspar and the radiate transformation-product of hornblende. The felspar has a specific gravity of 2.648; melts easily before the blowpipe, imparting a strong yellow colour to the flame; is attacked, but not completely decomposed, by hydrochloric acid:

SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	Na ² O	%
53.51	29.37	trace	12.78	1.54	3.10	= 100.30

The radiate transformation-product of the hornblende has a chloritic aspect, and is sharply separated from the latter, its fibres standing perpendicularly on the hornblende faces. Hardness = 2. Specific gravity = 2.997–3.057. Before the blowpipe it melts easily (not exfoliating, like the easily fusible chlorites) to a black, strongly magnetic bead. Analysis gave:

SiO ²	Al ² O ³	Fe ² O ³	Fe ² Cl	MnO	MgO	CaO	H ² O	%
32.78	15.60	29.90	2.98	1.15	4.90	6.74	7.52	= 101.57

whence may be deduced the formula—



By a comparison with other similar minerals, Bertels infers that this transformation-product of hornblende is a new species of the chlorite-group, for which he proposes the name *Phæactinite*, indicative of its grey-brown colour and radiate texture.

From a calculation of the total constituents of the rock, it is inferred that, whilst the porphyritically separated felspar is labradorite, the felspathic ground-mass consists of a more acid plagioclase. This remarkable association of a felspathic hornblende rock with nœsan and nephelin, in which the felspar is exclusively triclinic without a trace of orthoclase, gives the rock a distinct character. The similarity of isenite to the Etna lavas, indicated by the comparatively large crystals of porphyritically intergrown labradorite which it contains, is still more plainly seen in the chemical constitution, as shown by comparison with the mean of 28 analyses of Etna lavas.

The rock most nearly allied to isenite, though still different from it, is the *hauyn* nephrite from the Canaries, described by K. v. Fritsch and W. Reiss.

ISETHIONIC ACID, $\text{C}^2\text{H}^4\text{SO}^4 = \text{CH}^2\text{OH} \cdot \text{CH}^2\text{SO}^2 \cdot \text{OH}$. The chloride of this acid, $\text{CH}^2\text{OH} \cdot \text{CH}^2\text{SO}^2\text{Cl}$, is formed, together with the two isomeric compounds, *chlorisethionic acid*, $\text{CH}^2\text{Cl} \cdot \text{CH}^2\text{SO}^2 \cdot \text{OH}$, and *ethylsulphuric chloride*, $\text{C}^2\text{H}^5 \cdot \text{O} \cdot \text{SO}^2 \cdot \text{Cl}$, by the action of sulphuric anhydride on ethyl chloride (p. 746).

On the conversion of isethionic into ethionic acid, $\text{C}^2\text{H}^4\text{S}^2\text{O}^7$, by the action of sulphuric acid, see page 742.

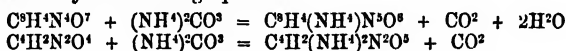
Action of Heat on Ammonium Isethionate.—This salt (m. p. 135°, or according to Strecker, 130°) remains unaltered when heated for several days on an oil bath at 210°–230°, but decomposes readily on raising the temperature of the saline mass to 230°–240°; and if, after the boiling has been continued for about eight hours, the resulting viscid syrup be dissolved in water, the solution boiled with animal charcoal and evaporated, the residue crystallised from alcohol, and the separated nodules, which are now almost insoluble in alcohol, constantly boiled with that liquid till they melt at 192°–193°, a compound is obtained which dissolves very easily in water, appearing indeed to be hygroscopic, gives off ammonia on addition of potash, and has the composition of taurine, $\text{C}^2\text{H}^4\text{NSO}^3$. Taurine, however, melts with decomposition at about 240°, and behaves in a different manner with potash (v. 700): hence the

compound formed by dehydration of ammonium isethionate is not identical, but isomeric with it, and appears indeed to be the true amide of isethionic acid (H. Seyberth, *Deut. Chem. Ges. Ber.* vii. 391).

ISODIPIC ACID. The crystalline compound which Meyer & Dulk obtained by the action of chloral on glacial acetic acid (*Ber.* iv. 963) is regarded by Hübner (*ibid.* vi. 109) as an isomeride of adipic acid, $C^8H^{10}O^4$.

ISOALLOXANIC ACID, $C^8H^4N^2O^5$. This modification of alloxanic acid—some of the salts of which were obtained by L. Hardy, by the action of bases on the red modification of alloxan produced by heating the latter to 260° (vi. 90)—has been further examined by Magnier de la Source (*Bull. Soc. Chim.* [2], xxii. 56), who obtains it by dropping bromine into water in which uric acid is suspended (1 part bromine to 40 or 50 parts water) till the liquid becomes clear. The whole is then transferred to a basin and heated over a water-bath in a stream of hydrogen, whereupon hydrobromic acid is abundantly evolved, the liquid becomes colourless, and a carmine-coloured precipitate is ultimately deposited on the sides of the vessel—apparently identical with the red modification of alloxan observed by Hardy. The solution above mentioned yields with baryta-water a splendid violet precipitate of barium isoalloxanate, which however cannot be obtained free from the colourless alloxanate, since it quickly passes into the latter on exposure to moist air. If ammonia be added in place of baryta-water, a fine purple colour is produced, and on subsequent addition of alcohol a red precipitate is formed, mixed with a large quantity of ammonium bromide; and on washing the precipitate with alcohol to remove the latter, and drying it in a vacuum, ammonium isoalloxanate is deposited in the form of a brick-red powder, very soluble in water, with which it forms a deep purple solution, very sparingly soluble in alcohol, insoluble in ether. Its solution gives with baryta-water a deep-red precipitate, with calcium chloride a rose-coloured precipitate, and with silver nitrate a precipitate of a fine indigo-blue colour; with carbonate of potassium or sodium a violet coloration, with cupric acetate a green coloration. The aqueous solution of the ammonium salt quickly loses its colour; the alcoholic solution, on the other hand, does not change colour perceptibly; the solid salt is permanent in dry air.

In accordance with these results it must be assumed that the so-called murexid reaction is due, on the one hand, to the formation of ammonium isoalloxanate, $C^8H^2(NH^4)^2N^2O^5$, and, on the other, to the formation of acid ammonium purpurate, $C^8H^4(NH^4)N^2O^6$. This latter compound is formed by treating alloxantin with ammonium carbonate, whereas the isoalloxanate is produced by similar treatment of alloxan, as shown by the following equations:



These two colouring matters are therefore formed simultaneously by the action of ammonium carbonate on a mixture of alloxan and alloxantin; the ammonium isoalloxanate may be partially removed by washing, but a portion of it is likely to remain mixed with purpurate, a circumstance which may account for the very different formulæ assigned by different chemists to murexid.

ISO-HEMIPINIC ACID. See NARCOTINE DERIVATIVES.

ISO-LEPIDENE. See LEPIDENE.

ISOBUTYL IODIDE. The conversion of this ether into tertiary butylamine, $(CH^3)_3C.NH^2$, by the action of dry silver cyanate—observed by Linnemann (vii. 223), but called in question by Hofmann (*Liebig's Annalen*, clxii? 19) who obtained chiefly isobutylamine—has recently been confirmed by Brauner (*ibid.* excii. 65), who operated with perfectly pure isobutyl iodide. On the properties of the butylamine thus obtained, see TRIMETHYLCARBINYLAMINE.

ISOBUTYLACETIC ACID. See PENTOIC ACIDS.

ISOBUTYLACETO-ACETATE, ETHYLIC. Respecting this compound and its derivatives, heptic acid, oxyheptic acid, and ethylic methylisobutylglycerate, see HEPATIC ACID (p. 1020).

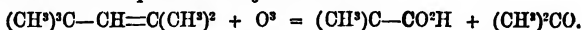
ISOBUTYLAMARIC ACID, $C^{30}H^{30}O^8$ (Zinin, *Deut. Chem. Ges. Ber.* x. 1735). This acid, homologous with amaric acid, $C^{46}H^{42}O^8$ (vii. 55),* is formed, similarly to the latter, by prolonged boiling of benzamarone with a solution of potash in isobutyl alcohol. It is nearly insoluble in water, but dissolves easily in ether and in alcohol, from which latter it crystallises in rhombic plates. It melts at 175° – 179° , and is thereby converted into an amorphous anhydride, $C^{30}H^{40}O^4$, which dissolves in ether,

* The formula there assigned to amaric acid is $C^{46}H^{40}O^8$, but subsequent experiments have shown that the true formula is that above given.

yielding, when treated with phosphorus pentachloride, the same chloride that is produced by the action of hydrochloric acid upon isodibutylene. It is a tertiary alcohol, its iodide, when treated with silver nitrite, giving neither a nitrolic nor a pseudonitrolic acid (Victor Meyer's test; see NITROPARAFFINS).

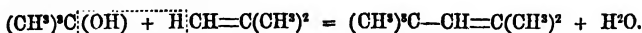
Isodibutyl submitted to the regulated action of oxidising agents, gave, besides unaltered alcohol and isobutylene, the same products that are furnished by oxidation of isodibutylene, but no ketone or aldehyde, a further proof that it is neither a primary nor a secondary alcohol. Its constitution may therefore be determined by studying the oxidation of isodibutylene. This body was accordingly treated in the cold for six days with a mixture of sulphuric acid and potassium dichromate, whereupon carbon dioxide was continuously evolved. The mixture was then distilled, that part of the distillate which contained oily drops being collected separately from the clear acid liquid which subsequently passed over. This clear liquid contained principally *acetic acid*. The first distillate was treated with potassium carbonate, whereby much of the oil was dissolved. The undissolved oil was removed, and the remaining alkaline liquid again distilled. From the first portions of liquid which then passed over *acetone* was easily separated by potassium carbonate in excess, not, however, in large quantity, probably because much of it had been oxidised to acetic acid. The alkaline solution, after removal of the acetone and oil, gave, on treatment with sulphuric acid, acetic and *trimethyl-acetic* acids. Since trimethyl-acetic acid does not give acetone on oxidation, it is thus evident that the primary oxidation-products of isobutylene are *acetone* and trimethyl-acetic acid, thus: $C^6H^{16} + O^3 = C^3H^{10}O^2 + C^3H^8O$. The acetone is partially oxidised to acetic acid.

This experiment establishes the constitution of isodibutylene. For of the two products one contains *three*, the other two, methyl groups; from which it must be inferred that the molecule of isodibutylene contains *five* such groups. Three of these must be united to one carbon-atom to form tertiary butyl, $(CH^3)^3C-$, which appears in the trimethyl-acetic acid, the remaining two methyls forming with another carbon-atom the group $(CH^3)^2C=$, which by oxidation yields acetone. From these considerations the formula of isodibutylene may be inferred to be $(CH^3)^3C-CH^2C(CH^3)^2$; and that of the corresponding tertiary alcohol, isodibutyl $(CH^3)^3C-CH^2C(CH^3)^2OH$. The oxidation of the hydrocarbon follows the general rule for the series C^6H^{2n} , viz. that the carbon-atoms separate at the junction $C=C$.



This constitution of isodibutylene granted, the mode of its formation from trimethyl-carbinol is the following: (1) part of the alcohol splits up into water and isobutylene; (2) one molecule of isobutylene unites with one of unaltered trimethyl-carbinol, water being again eliminated. The course of the reaction is quite analogous to Collarits' and Merz's synthesis of aromatic ketones by the action of phosphoric anhydride upon a mixture of a hydrocarbon and an acid, or to Wischnegradsky's synthesis of diamylene (p. 635).

To account for the second phase of the reaction, it must be remembered that methyl groups and their derivatives are in general less prone to enter into reaction than the groups $-CH^2$ or $\equiv CH$, and their derivatives. The different degrees of stability are well observed in the alcohols of the three categories and the bodies allied to them, the radicles of the primary alcohols being least inclined to part with the hydroxyl or other simple radicles united to them, while in the tertiary alcohols and their allies such separations take place with the greatest ease. When, therefore, trimethyl-carbinol is partially resolved into water and isobutylene, the feebly-bound hydroxyl of the undecomposed alcohol combines more readily with the hydrogen in the group $\equiv CH^2$ of the hydrocarbon than with that belonging to the more stable methyl groups of its own molecule, thus—

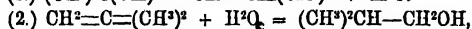


On the other hand, when isobutyl alcohol, $CH^2(OH)-CH(CH^3)^2$, separates partially into water and this same (iso-) butylene, no such condensation takes place, because the alcoholic hydroxyl unites with the hydrogen of the group $\equiv CH$ in its own molecule, rather than with that of the $\equiv CH^2$ of isobutylene.

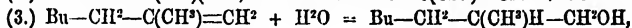
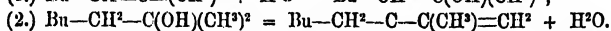
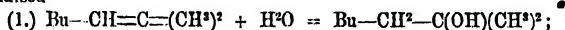
These considerations, somewhat modified, will also explain why secondary butyl alcohol, on treatment with sulphuric acid, gives, as a principal product, pseudo-butylene, but no dibutylene. Here the alcoholic hydroxyl tends to combine either with the hydrogen of the pseudo-butylene, $CH^3-CH=CH-CH^3$, first formed, or with that of the $\equiv CH^2$ in its own molecule. The proximity of the latter determines its union with it, and consequently the complete conversion of the alcohol into pseudo-butylene.

The higher-boiling portions of the oily acids from the oxidation of isodibutylene

were found to consist of trimethyl-acetic acid and a new octoic acid, $C^8H^{16}O_2$, the separation of which was ultimately effected by preparing the cadmium salts, and fractionally distilling the acids extracted from them. This octoic acid is a colourless oily liquid, smelling like trimethyl-acetic acid, and boiling with partial decomposition at 205° – 218° . Its constitution is best expressed by the formula, $C(CH^3)_3-CH^2-OH(CH^3)COOH$; since the carboxyl group must be formed at the expense of one of the five methyl groups of isodibutylene, and it is reasonable to assume that the group oxidised is one of those lying nearest to the point of attack of the oxidising agent, viz. the doubly united carbon-atoms $C=C$. The formation of this acid from isodibutylene appears strange at first sight, but is not without analogy, since oxidation of the hydrocarbons C^8H^{16} appears in general to furnish the same products as that of the corresponding tertiary alcohols. Thus it is found that a certain quantity of isobutyric acid may be obtained by oxidation of trimethyl-carbinol. Now this octoic acid may be regarded as isobutyric acid in which hydrogen is displaced by tertiary butyl $(CH^3)_3C-$, isodibutol and isodibutylene being similarly derived from trimethyl-carbinol and isobutylene respectively. It may be assumed that, in both cases, by the successive removal and addition of water, an isomeric alcohol is first produced, which is then oxidised to the acid. Thus, when trimethyl-carbinol is oxidised—



which furnishes isobutyric acid, $(CH^3)_2CH-CO^2H$; and when isodibutylene is oxidised—



which yields the above octoic acid.

This explanation is supported by the fact that one of the oxidation-products of isodibutylene is a body derived from the octylene, $C(CH^3)_3-CH^2-C(CH^3)=CH^2$, whose existence is assumed in equations (2) and (3). This hydrocarbon would, upon oxidation, separate at the doubly-jointed carbon-atoms, and give, as a first product, a ketone, $C(CH^3)_3-CH^2-CO-CH^2$; and, in fact, the oily products insoluble in potassium carbonate were found to consist of a mixture of isodibutylene, and a ketone of this composition boiling between 125° and 130° . The peculiar deportment of this body with metallic sodium is also exhibited by an undoubted ketone, namely, *ethylisopropyl ketone*, prepared by acting with zinc-ethyl on isobutyryl chloride; these bodies do not attack the sodium in the cold, but dissolve it rapidly when warm, giving solutions which, in contact with air, quickly assume a blood-red colour, finally passing into brown. On the other hand, the body in question is not oxidised by silver oxide; it does not combine with acid sodium sulphite; nor does it throw down ferric hydrate when boiled with ferric chloride, properties which distinguish it from the aldehydes and the oxides of the class to which ethylene oxide belongs. Finally, when oxidised with sulphuric acid and potassic bichromate, it yields acetic and trimethyl-acetic acids, as follows:—



This reaction is decisive with respect to its constitution.

The views above developed receive some support from Butlerow's observations on the action of sulphuric acid upon pentylene (trimethylated ethylene) from tertiary pentyl alcohol. Here the successive assimilation and separation of water take place without any change in position of the hydroxyl. In the cold sulphuric acid converts this pentylene into dipentylene. But when tertiary pentyl alcohol is heated to 100° in a tube with three times its volume of a mixture of equal weights of sulphuric acid and water, the principal product is uncondensed pentylene, which floats on the surface of the acid. If now the tube be laid on its side for some days, and occasionally shaken, the hydrocarbon again dissolves, i.e. assimilates water to reproduce the alcohol; and these operations may be repeated several times. Here, then, is an example of dissociation, and of gradual reunion of the dissociated bodies to form the original compound. In the case of isodibutol, on the other hand, the dissociated products (isodibutylene and water) would reunite to form, not the original alcohol, but an isomeric.

ISODULCITE, $C^8H^{16}O^6$. This crystalline sugar, isomeric with dulcitol and mannitol, which Hlasiwetz a. Pfaundler obtained by the action of dilute acids on quercitrin (v. 1091), is likewise produced by similar treatment of the glucoside of buckthorn berries (*Rhamnus infectoria*). Liebermann a. Hörmann, who obtained it

from this source (*Berl. Ber.* xi. 952), regarded it as a peculiar sugar, different from isodulcite, and named it *rhammodulcite*, inasmuch as they found its melting point to be 92° – 93° , whereas isodulcite from quercitrin was said by Hlasiwetz a. Pfaundler to melt at 105° . Berend, however (*ibid.* 1353), on re-examining the isodulcite obtained from quercitrin, finds that it melts at 93° – 94° , and further that it agrees exactly with the sugar obtained by Liebermann a. Hörmann in crystalline form and in specific rotatory power; $[\alpha]_D = +8.04$ (Berend); $+8.07$ (L. and H.) The name *rhammodulcite* may therefore be dispensed with. 1 pt. isodulcite dissolves, according to Hlasiwetz a. Pfaundler, in 2.09 pts. water at 18° ; according to Liebermann a. Hörmann, in 1.8 pts. (mean of three experiments; temperature not stated).

Isodulcite heated with concentrated hydriodic acid is in great part converted into a tarry mass, and yields a heavy liquid distillate containing iodine and consisting of a mixture of bodies, none of which have yet been obtained in the pure state (Dale a. Schorlemmer, *Ber.* xi. 1197).

ISOFERULIC ACID. See VANILLIN-DERIVATIVES.

ISOHEMIPINIC ACID. See NARCOTINE-DERIVATIVES.

ISOLEPIDENE. See LEPIDENE.

ISOMERISM. Compounds of the same elements in the same proportions, and of the same molecular weight, but having different properties, may be said to be *isomeric*, if from the manner in which they are formed and from their reactions, it may be concluded that they are bodies of the same type; if their behaviour indicates that they are bodies of different type, they may be said to be *metameric*.

A perusal of modern chemical literature shows that the term 'isomeric' is on the whole very loosely employed, some writers attaching a much more extended meaning to it than others; the foregoing definition is probably both the most restricted and the most extended that can well be given. The only difficulty which can arise in connection with it is that of determining whether two or more compounds more or less different in properties are bodies of the same type. If, however, a too formal construction of the phrase be avoided, this difficulty is a very slight one. For example, the hydrocarbons ethyl-benzene and the three dimethyl-benzenes or xylenes not only exhibit a very close general resemblance in behaviour, especially in the formation of substitution-compounds, but are also immediate derivatives of the same parent hydrocarbon, benzene: they may hence be regarded as bodies of the same type—i.e. as isomerides, although their behaviour with oxidising agents clearly indicates that ethyl-benzene differs to a much greater extent from the xylenes than these latter differ amongst themselves; a fact which finds an expression in the rational formulæ assigned to the several hydrocarbons. On the other hand, benzene and the hydrocarbon dipropargyl discovered by Henry differ so totally in properties that we without hesitation regard them as compounds of different type, i.e. as metamerides. Again, the four butylic alcohols or hydroxides of the formula $C^4H^9.OH$ are isomeric with each other, but metameric with methyl-propyl oxide, methyl-isopropyl oxide and diethyl oxide or ordinary ether, these last three oxides being isomeric with each other.

As the rational formulæ we employ are merely condensed symbolic expressions, affording more or less complete information as to the characteristic chemical properties of the compounds which they represent, especially with regard to the manner in which they are formed and in which they undergo change when submitted to the action of reagents, compounds which differ either in their mode of formation or in their behaviour under similar circumstances are necessarily represented by different rational formulæ. Recent investigations have, however, conclusively shown that a by no means inconsiderable number of 'isomeric' compounds exist, many of them widely different in so-called physical properties, which exhibit so close a resemblance in general chemical properties that, following the canons of the present system of notation, they can only be represented by identical formulæ.

The hydrocarbons of the formula $C^{10}H^{16}$, which occur in various essential oils, are the only instance of this kind that we meet with among the hydrocarbons, but a more striking instance can scarcely be advanced. At least, two classes of these hydrocarbons may be distinguished: those boiling at about 156° , which are conveniently termed terpenes; and those boiling at about 176° , which may be termed citrenes, as they are the chief constituents of the oils derived from the various species of *Citrus*. Each of these classes includes a considerable number of species which appear to differ only in their behaviour towards polarised light; in fact, up to the present time no two oils have been proved to contain the same terpene or citrene. It is highly probable, however, that many which are now regarded as distinct substances will be found to be mixtures, and that the number of separate species is not nearly so great as has been supposed; but the existence of lævo- and dextro-

rotatory members in both classes is sufficient proof that there are several of each. At present the experimental evidence is not sufficient to enable us to say whether the terpenes and citrenes have identical formulæ. Their behaviour with hydrochloric acid would appear to favour the conclusion that they have not, inasmuch as the former furnish monohydrochlorides, and the latter dihydrochlorides. But, on the other hand, they have the same combining power, as they form tetrabromides; they yield identical oxidation-products* (Fittig); they yield nitrosochlorides and nitroso-substitution compounds differing only in physical properties; and they are convertible into the so-called terpin, from which, by the action of hydrochloric acid, the corresponding dihydrochloride is obtained: so that indirectly the terpenes, as well as the citrenes, may be converted into dihydrochlorides, and that too by reactions taking place at ordinary temperatures and involving no violent treatment.*

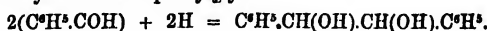
It is impossible at present to assign a rational formula to the terpenes and citrenes which is consistent with their general behaviour; all those hitherto proposed appear to be insufficient.

The camphenes or solid hydrocarbons of the formula $C^{10}H^{16}$, which also exist in several modifications, differing only in their behaviour in polarised light, are undoubtedly bodies of an altogether different type, as they have only half the combining power of the terpenes and citrenes, and are directly converted into camphor by oxidation. Both dextro- and lævo-rotatory and optically inactive modifications of this last-named body are also known.

Among the haloid-derivatives of hydrocarbons, no instances of isomerism similar to those just discussed have been met with; a number of haloïd-nitro-derivatives of benzene, however, have been shown to exist in several modifications differing in crystalline form and melting point, but readily convertible into each other. Thus, according to Jungfleisch, two dinitrochlorobenzenes may be obtained by nitration of chlorobenzene, one of which is converted into the other by merely bringing the two kinds of crystals into contact, the reverse change being effected by suddenly cooling the fused substance (vii. 145). Two modifications of nitrotetrabromobenzene exhibiting a similar behaviour have been described by v. Richter (viii. 182). Laubenheimer (*Dent. Chem. Ges. Ber.* ix. 766) states that metachloronitrobenzene exists in two forms, differing about 20° in melting point; and that no fewer than three crystalline modifications, and probably a fourth liquid modification of nitrometachloronitrobenzene may be obtained (viii. 183). A number of similar instances have been observed among oxygenated compounds of other classes. Thus Zincke has described two modifications of diphenyl-ketone or benzophenone (vii. 176), two modifications of tolylphenyl-ketone, and also two modifications of the diacetate from isohydrobenzoïn; and Tollens has shown that dibromopropionic acid, $CH^2Br.CHBr.COOH$, may be obtained crystallised in two forms of different melting point. It appears probable, as Laubenheimer has suggested (*Ber.* ix. 766), that the existence of these modifications is due to the formation of aggregates of the ultimate molecules of different degrees of complexity, the crystals being regarded as built up of such aggregates; and if it be assumed that the stable modifications consist of aggregates of lesser, and the unstable modifications of aggregates of greater complexity, we have an explanation of the fact that the melting point of the stable modification is always higher than that of the unstable, and that the unstable modification is formed by heating the substance. If such be the nature of these modifications, however, it appears desirable that they should be spoken of as physical modifications, and not as physical isomerides.

It is chiefly among the alcohols and acids that we meet with well-marked instances of isomerism which cannot apparently be explained by our present theory. The instances alluded to are, in the case of the alcohols, the diphenylglycols, hydrobenzoïn and isohydrobenzoïn, and the hexhydric alcohols, mannitol (mannite) and dulcitol (dulcite); the glucoses, which are closely related to the two latter alcohols, afford additional examples.

Hydrobenzoïn and isohydrobenzoïn are formed simultaneously by reduction of benzaldehyde, and therefore the most probable formula that can be assigned to them is that of a symmetrical diphenylglycol:



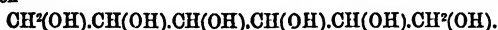
This formula is confirmed, and the possibility of isomeric change having taken place in the formation of either is precluded by the fact that both furnish benzaldehyde on oxidation, almost in the proportion required by the equation:



* Quite recently Tilden has shown that the terpenes may be directly converted into dihydrochlorides, by submitting them to the action of hydrochloric acid when dissolved in alcohol, ether, or acetic acid. Except sylvestrene, all the various terpenes and citrenes furnish the same dihydrochloride.

The only other possible formula which could account for this behaviour on oxidation, viz. $C^6H^2.C(OH)^2.CH^2.C^6H^4$, cannot be assigned to either of them, on account of their comparative stability, all known compounds in which two hydroxyl groups are associated with the same carbon-atom being highly unstable bodies. Further evidence of the identity of the two alcohols from a chemical point of view is afforded by their behaviour with phosphoric pentachloride and with dilute sulphuric acid; the former reagent converts each into a chloride of the formula $C^{14}H^{12}Cl^2$, but the products from the two sources are identical; when boiled with the latter, both furnish diphenyl-acetaldehyde, $(C^6H^5)^2HC.CO.H$, and a crystalline non-volatile body of the formula $C^{14}H^{12}O$, the body of this formula obtained from the one being however isomeric with that obtained from the other, and apparently in the same sense that the parent alcohols are isomeric (Forst a. Zincke, *Liebig's Annalen*, clxxxii. 241; Zincke and Breuer, *Deut. Chem. Ges. Ber.* ix. 1769).

The evidence that mannitol and dulcitol must have identical formulæ assigned to them is equally strong. By their conversion into secondary hexylic iodide (Hecht), $CH^2.(CH^2)^2.CH.I.CH^2$, both are proved to be derivatives of normal hexane; and as they are compounds of relatively very considerable stability, each of the hydroxyl groups must be regarded as associated with a distinct carbon-atom, so that their formula must be written



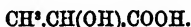
If this be the case, the only possible formula for the glucoses, dextrose, lævulose and galactose—supposing them to be bodies of identical molecular weight—is the following:



since they are penthydroxylated compounds, and are directly convertible into mannitol or dulcitol by the action of nascent hydrogen.

Passing now to the acids, we have to notice the examples afforded by the lactic acids, by malic and tartaric acids, by mucic and saccharic acids, by the hydromellitic acids, by the crotonic acids and a number of their homologues, by malic and fumaric acids and their homologues, and by the camphoric acids.

The researches of Wislicenus have shown that a modification of ordinary lactic acid exists which differs from the latter only in that it is optically active: in their chemical reactions the two modifications are precisely similar, and both can be represented only by the formula



Several modifications of malic acid exist, apparently corresponding with the several modifications of tartaric acid, viz. a lævorotatory modification, which occurs naturally, a dextrorotatory modification, formed by partial reduction of tartaric acid (Dessaignes, Bremer), and one at least optically inactive modification (Loydl, *Liebig's Annalen*, xciii. 80). Theory admits only of the existence of a single acid of the formula



Tartaric acid, it is well known, exists in four distinct modifications. Racemic acid is no doubt a body of different molecular weight from either lævo- or dextro-tartaric acid, and it is not impossible, although improbable, that mesotartaric acid is also; but lævo- and dextrotartaric acid are undoubtedly isomeric. There is, however, only one formula which can be assigned to a body behaving like dextro- and lævo-tartaric acid, viz.

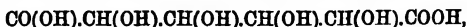


the alternative formulæ,

, $COOH.CH^2.C(OH)^2.COOH$ and $CH^2(OH).C(OH)(COOH)^2$ or $CH(OH)^2.CH(COOH)^2$, are entirely out of the question.

The camphoric acids obtained by oxidation of the various modifications of camphor, like the parent substances, appear to differ only in their optical characters.

Saccharic and mucic acids being derived from mannitol and dulcitol respectively, and being directly obtained therefrom by oxidation, must both be represented by the formula



which also is in accord with their general behaviour.

Hydro- and isohydromellitic acids, $C^6H^4(COOH)^2$, afford another instance of two compounds which apparently must be represented by identical formulæ. The former undergoes slow spontaneous conversion into the latter when kept, and the change is easily effected by heating with strong hydrochloric acid solution at 180° . The carboxyl groups in hydromellitic acid must be regarded as each associated with a different carbon-atom, and Baeyer assumes that the conversion into the iso-acid is the

result of the transposition of one of the carboxyl groups. But the fact that the iso-acid is an extremely stable body, and far more stable than mellitic acid, entirely negatives the assumption that more than a single COOH-group is associated with a single carbon-atom.

Crotonic acid being represented by the formula $\text{CH}^3.\text{CH}=\text{CH}.\text{COOH}$ —on account of its formation from acetaldehyde and of its behaviour on oxidation, and methacrylic acid by the formula $\text{CH}^2=\text{C}(\text{CH}^3).\text{COOH}$ —because of the production of a mixture of formate and propionate on fusing it with potassium hydroxide, isocrotonic or quartenylic acid (vii. 397; viii. 586), has been represented by the third of the three formulæ possible for an acid of the composition $\text{C}^4\text{H}^5.\text{COOH}$, viz.



Recent investigations, however, throw considerable doubt on the correctness of this conclusion, and render it extremely probable that both crotonic and isocrotonic acids must be represented by the same formula. Thus the formation of acetate alone on fusing it with potassium hydroxide, instead of a mixture of formate and propionate, has been 'explained' by the assumption of a previous isomeric change similar to that which occurs on heating the acid; but, apart from the fact that the conversion of isocrotonic into crotonic acid is not complete even after prolonged heating at 170° – 180° (Alberti), it has been shown that similar products (formic, acetic and oxalic acids) are obtained when the oxidation is effected entirely without the aid of heat by permanganate (Hemilian, *Liebig's Annalen*, clxxiv. 330). It may be argued that the conversion of an acid of the formula $\text{CH}^2=\text{CH}.\text{CH}^2.\text{COOH}$ into that of the formula $\text{CH}^3.\text{CH}=\text{CH}.\text{COOH}$ is not without analogy, and is therefore probable, since allylic alcohol, $\text{CH}^2=\text{CH}.\text{CH}^2.\text{OH}$, yields solid crotonic acid, $\text{CH}^3.\text{CH}=\text{CH}.\text{COOH}$, when the cyanide prepared from allylic iodide by double decomposition with potassic cyanide is digested with alkali, &c.; the oxidation-products of allylic alcohol and iodide, and of the cyanide and crotonic acid which they furnish, are, however, very different, no acetic acid being obtained from either of the former (Kekulé and Rinne, *Deut. Chem. Ges. Ber.* vi. 386),* and it appears improbable that an acid having the constitution $\text{CH}^2=\text{CH}.\text{CH}^2.\text{COOH}$ would furnish acetic acid on oxidation.

If crotonic and isocrotonic acids have identical formulæ, the two chlorocrotonic acids obtained from ethyl acetoacetate must also be represented by identical formulæ.

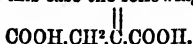
Cinnamic acid, $\text{C}^9\text{H}^7.\text{CH}=\text{CH}.\text{COOH}$, the analogue of crotonic acid in the aromatic series, affords another instance of isomerism requiring further elucidation. According to Glaser, the dibromide of this acid yields two isomeric (α and β) bromocinnamic acids; that of lower melting point (β) is converted into that of higher melting point by mere distillation or by heating with hydriodic acid, and Barisch has recently shown (*J. pr. Chem.* [2], xx. 173) that the ethyl salt prepared from the β -acid is identical with that obtained from the α -acid. The α -acid being represented by the formula $\text{C}^8\text{H}^5.\text{CBr}=\text{CH}.\text{COOH}$, the only other possible formula for an acid formed in such a manner, viz., $\text{C}^8\text{H}^5.\text{CH}=\text{CBr}.\text{COOH}$, is assigned to the β -acid, but it must be admitted that direct evidence of the correctness of this formula is wanting. The formation of cinnamic acid from both α - and β -bromocinnamene by the action of sodium and carbonic anhydride is also remarkable.

The isomerism of angelic and methylcrotonic acids, $\text{C}^4\text{H}^5.\text{COOH}$, is also highly remarkable. The former is converted into the latter by mere distillation. Both furnish the same products on fusion with potassium hydroxide, when combined with hydrobromic acid, or when combined with bromine, but dissimilar iodovaleric acids when united with hydriodic acid (compare Demarçay, *Compt. rend.* lxxx. 1400; lxxxiii. 906; Fittig, Kopp and Pagenstecher, *Liebig's Annalen*, xciv. 81–128; Schmidt, *Deut. Chem. Ges. Ber.* xii. 252). The dibromide prepared from angelic acid is deprived of its bromine by distillation or by the action of nascent hydrogen: the parent acid is not regenerated, however, but methylcrotonic acid is produced instead. This behaviour can be represented in accordance with our present symbolic system of notation only by assigning the same formula to the two acids.

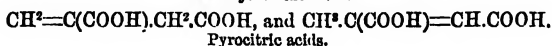
Lastly, it appears probable that the difference between oleic and elaidic acid is of the same order as that which obtains between the crotonic acids and between angelic and methylcrotonic acid, as they furnish the same products on fusion with potassic hydroxide, and are both converted into stearic acid by the withdrawal of 2 atoms of hydrogen.

Passing to the bibasic acids, fumaric and maleic acid and their homologues, citraconic and mesaconic acids, are apparently also to be included in the category of exceptions. As fumaric and maleic acid do not lose carbon dioxide when heated, and both yield ordinary succinic acid when treated with nascent hydrogen, we must assume that in both the carboxyl groups are associated with different carbon-atoms; but there is only one formula possible satisfying this condition, viz., $\text{COOH}.\text{CH}=\text{CH}.\text{COOH}$.

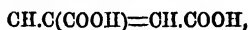
unless indeed we assume as Kekulé and more recently Fittig have suggested (*Liebig's Annalen*, clxxxviii. 95) that in the so-called unsaturated compounds the affinities of the carbon-atoms which are not engaged with other elements need not necessarily mutually satisfy each other: in this case the following formula is also possible,



Again, there are only two formulæ by which the pyrocitric acids, itaconic, citraconic and mesaconic acid can be represented, since each is converted into methylsuccinic (pyrotartaric) acid when submitted to the action of nascent hydrogen, thus:



Itaconic acid is most probably represented by the first of these formulæ, as it yields allene, $\text{CH}^2=\text{C}=\text{CH}^2$, on electrolysis; only one formula therefore remains for both citraconic and mesaconic acid, but this accords entirely with their general behaviour and especially with the fact that both furnish methylacetylene (allylene) on electrolysis. If, however, we admit the 'unsatisfied affinity' hypothesis, we may, as Fittig suggests, represent the one acid by the formula



the other by the formula



But although this hypothesis appears to be applicable in the case of these acids, and also in the case of the acids of the acrylic series before alluded to, it does not enable us to explain the isomerism of mannitol and dulcitol, of the two hydrobenzoins, of the hydromellitic acids, or of the two tartaric acids of opposite rotatory power, which are all saturated compounds: this being so, it appears desirable to seek farther for an explanation which shall include the whole of the exceptions we have referred to, and not to accept one which is only of very limited application.

Two other remarkable instances of isomerism yet remain to be noticed: that afforded by the methylethylsulphine-compounds, and that afforded by certain hydroxylamine derivatives.

Thus, according to Krüger (*J. pr. Chem.* [2], xiv. 193), the sulphur metho-diethiodide, $\text{CH}^3.\text{S}(\text{C}^2\text{H}^5)_2\text{I}$, obtained by combining methyl iodide with ethyl sulphide, not identical with the body of the same composition produced by combining ethyl iodide with methyl-ethyl sulphide: the former compound and all the simple salts prepared from it by displacing the iodine by other negative radicles being so extremely soluble and deliquescent as to be uncrystallisable, whereas the latter crystallises readily in long needles, and furnishes a series of double salts which are all deeper in colour, of different crystalline form, and have lower melting points than those of the same composition derived from the body prepared in the manner first described; moreover, the chloride obtained from the former furnishes with mercuric chloride a double chloride of the formula $\text{S}(\text{C}^2\text{H}^5)_2(\text{CH}^3)\text{Cl.6HgCl}^2$, while that from the latter yields only a double chloride of the formula $\text{S}(\text{C}^2\text{H}^5)_2(\text{CH}^3)\text{Cl.2HgCl}^2$.

If the formula generally assigned to hydroxylamine be correct, viz. $\text{N}'''\text{H}^2.\text{OH}$, at most two isomeric derivatives should be obtainable from it, and the only alternative formula by which its relation to ammonia can be expressed, $\text{N}''\text{OH}^3$, does not admit of the existence of any isomerides. Lossen, however, has shown that by varying the order in which benzoyl and anisyl are introduced in place of the three hydrogen-atoms no fewer than *three* isomeric dibenzoylanisyl and *three* isomeric dianisylbenzoyl derivatives may be obtained, all but one of which moreover are dimorphic, one being even trimorphic (comp. pp. 1075-1079).

The formulæ of our present system are all constructed on the hypothesis that the several units of affinity of a polyad atom such as that of carbon, sulphur, or nitrogen, are of the same value and have identical functions. If it be assumed that this is not the case, the anomalies above noticed would appear at once to meet with an explanation. But such an explanation cannot be regarded as satisfactory, or even probable, when it is remembered that none of the simpler derivatives of methane, ammonia, &c., exist in a greater number of modifications than our theory requires, the anomalous bodies being all of comparatively complex composition; and that, according to this view, the number of possible isomerides would be very greatly in excess of that required by the present hypothesis: this latter argument being almost without doubt perfectly valid, as our knowledge of the simpler compounds, though necessarily

far from complete, is sufficiently advanced to warrant the conclusion that if such are really capable of existing, they would long ere this have been discovered. In fact, all things considered, the agreement between theory and practice is wonderfully complete, and this alone suggests that our present system must be a very close approximation to the true system.

Again, if it be assumed that our present formulæ are not merely symbols indicating the chief chemical characteristics of the compounds to which they refer, but that they are really representative of the relative mode of arrangement of the atoms in the compounds, it may be supposed that, even if the hydrogen-atoms in a compound such as methane are of equal value, isomeric derivatives are still possible, since the radicles introduced in place of the hydrogen-atoms may occupy relatively different positions in the molecules; thus two di-derivatives of the form $CRRR_1R_1$ (figs. 8 and 9), two of the form $CRRR_1R_2$ (figs. 10 and 11), and no fewer than three of the form $CRR_1R_2R_3$ (figs. 12, 13, and 14) would appear to be possible, R , R_1 , R_2 and R_3 being different monad radicles. Moreover, the group R_4 in the formula $CRRRR_1$ (fig. 15), has obviously on this hypothesis a different value from that of the group R , so that in a compound such as chloromethane, CH^3Cl , one of the hydrogen-atoms should have a special value. Conclusions of this kind are so entirely opposed to all experience, that they may be regarded as out of the question.

FIG. 8.

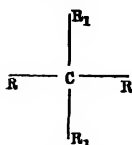


FIG. 9.

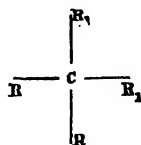


FIG. 10.

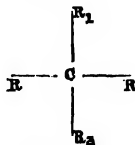


FIG. 11.

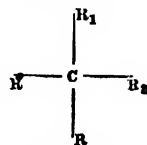


FIG. 12.

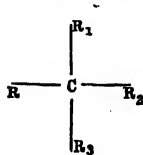


FIG. 13.

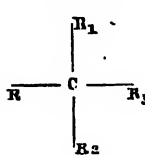


FIG. 14.

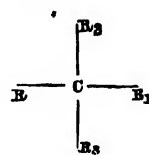
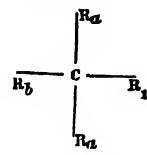


FIG. 15.



Van' t Hoff has proposed a system of formulæ based on the arrangement of the symbols in space, instead of in a single plane, which indicates a greater number of isomerides than our present system, and to which the objection above made does not apply (Van' t Hoff, *La Chimie dans l'Espace*, 1875; comp. *Die Lagerung der Atome im Raume*, a German adaptation of Van' t Hoff's pamphlet, by Herrmann, 1877). Similar views have also been advanced by Le Bel (*Bull. Soc. Chim.* xxii. 337, comp. *ibid.* xxiii. 295).

The fundamental hypothesis of the Van' t Hoff system consists in supposing that the carbon-atom occupies the centre of a tetrahedron, and that its four affinities are directed towards the four solid angles. The compounds of the forms $CRRRR$, $CRRRR_1$, and $CRRR_1R_2$, cannot exist in isomeric modifications, as in these cases a difference in the relative positions of the various radicles is not conceivable, but when all four radicles associated with the carbon-atom are different, two isomerides are possible, represented by figs. 16 and 17.

FIG. 16.

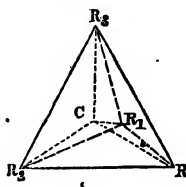
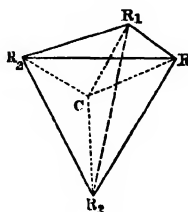


FIG. 17.

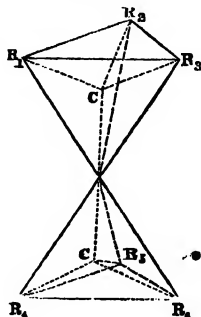


An observer lying along the edge R_1R_2 , having his head at R_2 , would in the one case (fig. 16) see R_1 on his right hand, and in the other on his left hand: the two

tetrahedrons bearing to each other precisely the relation of an object to its reflected image, and whatever the position in which they are placed, they cannot be superposed. A carbon-atom in this condition is termed *asymmetric*, and its presence in a formula may be indicated by an italicised *C*.

A combination of two carbon-atoms, associated by a single affinity of each, is represented by two tetrahedrons joined together, as in fig. 18.

FIG. 18.



Supposing the four corners R_1, R_2, R_4, R_6 of this figure to be in the same plane, and folding down the triangles $R_1R_2R_3, R_4R_5R_6$ in this plane, we have in fig. 19 a simpler symbol of such a combination.

FIG. 19.

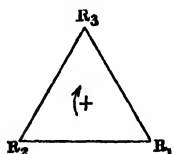


FIG. 20.

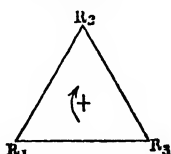


FIG. 21.

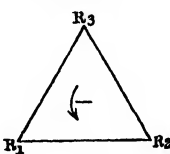


FIG. 22.

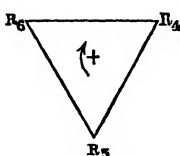
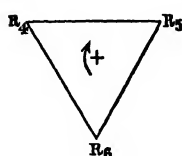
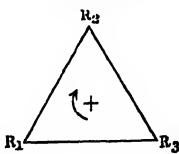


FIG. 24.

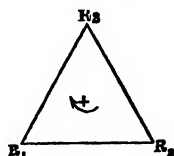
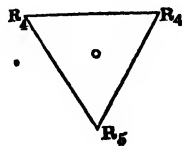
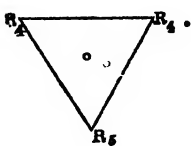
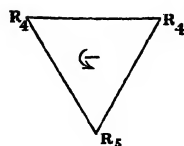
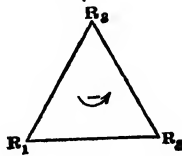


FIG. 25.



If we regard the system as rotating round an axis joining the two carbon-atoms, figs. 19 and 20 obviously do not represent isomerides, but merely the same combination at two phases of the rotation; this is not the case, however, with figs. 20 and 21, which differ in that the rotation of the groups $R_1R_2R_3$ is in one (or +) direction in the one case and in an opposite (or -) direction in the other. Denoting the order of rotation $R_1R_2R_3$ by the symbol +A, and rotation in the opposite direction by the symbol -A, and the rotation of the groups $R_4R_5R_6$ in like manner by +B and -B, the following different forms are, in fact, possible:

$$\begin{array}{cccc} +A & -A & +A & -A \\ +B & +B & -B & -B \end{array}$$

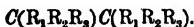
These are represented by figs. 20, 21, 22, and 23. If, however, only one of the carbon-atoms be asymmetric, the number of possible isomerides is reduced to two (figs. 24 and 25), since the order of succession of the radicles associated with the one carbon-atom cannot be varied, and therefore $+B = -B$: so that, in short, a compound of whatsoever kind in which the carbon-atoms are united by single affinities may be expected to exist in two isomeric modifications if it contain a single asymmetric atom of carbon; and if it contain two such atoms of carbon, four modifications would appear to be possible. By similar reasoning it may be shown that a compound containing three asymmetric atoms of carbon may exist in eight modifications, viz.:

$$\begin{array}{cccccccc} +A & +A & +A & +A & -A & -A & -A & -A \\ +B & -B & +B & -B & +B & -B & +B & -B \\ +C & +C & -C & -C & +C & +C & -C & -C \end{array}$$

one containing four in sixteen modifications; one containing five in thirty-two; and generally, that a combination containing n asymmetric atoms of carbon may exist in $(2)^n$ modifications, or

$$N_i = 2^n.$$

If the compound be represented by a symmetrical formula, however, the number of possible isomerides is somewhat less. The simplest case of this kind is represented by the formula



Here $A = B$, and the following different groupings at first sight appear possible,

$$\begin{array}{cccc} +A & +A & -A & -A \\ +A & -A & +A & -A \end{array}$$

but it is easy to see, especially if the figs. 26, 27, 28, 29, representing these groupings, are inspected, that

$$\begin{array}{c} +A \\ -A \end{array} = \begin{array}{c} -A \\ +A \end{array}$$

the one being merely the reversal of the other in space, and therefore the number of possible isomerides in such a case is reduced to three.

FIG. 26.

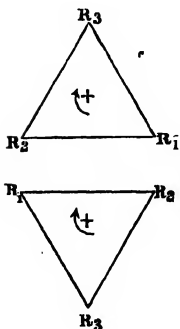


FIG. 27.

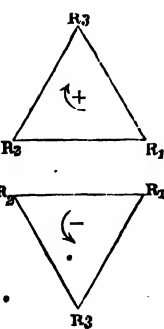


FIG. 28.

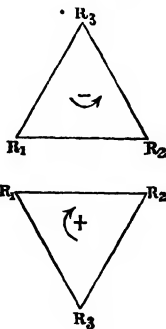
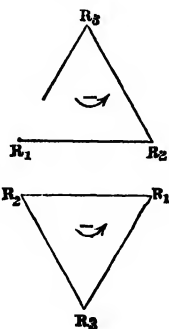


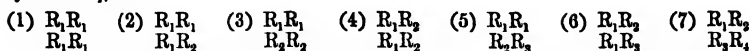
FIG. 29.



A less simple case is the following:



which may be produced being represented by the following arrangements of the symbols R_1 , &c. :



only those numbered 4, 6, and 7 may be expected to exist in two isomeric modifications.

The hypothesis does not indicate a greater number of isomerides than our present theory in the case of compounds in which the carbon-atoms are united by three affinities of each, or in the case of the benzene derivatives.

Van't Hoff has pointed out (*op. cit.*) that the isomerism of hydrobenzoin and isdrobenzoin, of the two lactic acids, of the two dibromosuccinic acids, of fumaric and maleic acids, of citraconic and mesaconic acids, of erotonic and isocrotonic acids and the corresponding chlorocrotonic acids, and of oleic and elaidic acids may be explained on the above hypothesis; and the additional instances that have been cited above, including the sulphine compounds, but not the hydroxylamine derivatives, would also appear to meet with an explanation, if such a hypothesis be admitted.*

There is, however, an objection of considerable force to any such hypothesis, that it does not satisfactorily account for the very considerable difference in properties between many of the bodies instanced, such as the hydrobenzoin, mannitol and ducitol, the glucoses, angelic and methylecrotonic acids, &c. As van't Hoff himself admits, isomerides differing in 'constitution' only in the manner described might be expected to differ in a comparatively slight degree and chiefly in certain physical properties; but there is a most distinct and often very considerable difference in so-called chemical properties between many of the bodies in question, dextrose and lævulose, for example, the latter undergoing fermentation less readily than the former, and yielding when digested with dilute sulphuric acid, acetopropionic acid, which is not produced from dextrose. If, as appears probable, the influence which a given substance exercises on the polarised ray is due to the molecules themselves, and is to a great extent independent of intermolecular action, it is conceivable that between bodies differing only in such a manner in constitution, there should be a difference such as that observed between dextro- and lævo-tartaric acid; but it is almost impossible to admit that there should be so substantial a difference in physical properties, such as melting and boiling point, which are chiefly dependent on intermolecular action, or on so-called chemical properties, as exist between many of the isomerides we have mentioned.†

In fine, whatever the imperfections of the present system of notation, it does not appear that any modification yet suggested is better adapted to the end in view; and it may be doubted, whether a more perfect system can be devised which does not take into account the dynamics of the molecules, and especially the loss or gain of energy involved in the passage of one system into another in similar reactions of isomerides.

H. E. A.

ISONITROBUTANE. See NITROPARAFFINS.

ISO-OXYCUMIC ACID, $C^{10}H^{12}O^3 = C^1H^1(CO^2H.O^3H.C^4H^1)$ (Jacobsen, *Deut. Chem. Ges. Ber.* xi. 1058). This acid is formed by prolonged fusion of carvacrol with potash; it may be purified by acidifying the crude product and distilling it in a current of steam; and separates out in flat needle-shaped crystals on adding hydrochloric acid to a solution of one of its salts. It melts at 93° , is only slightly soluble in cold water, but dissolves freely in hot water, also in alcohol, ether, and chloroform. The cold aqueous solution gives a deep red-violet colour with ferric chloride. The barium salt crystallises in anhydrous rhombic tablets, slightly soluble in water. The calcium salt, also anhydrous, crystallises in very soluble silky needles. The potassium salt is very soluble in water, but crystallises well; its concentrated solution gives with ferric chloride a dirty violet precipitate which dissolves in a large quantity of water with a fine red-violet colour; no precipitate or coloration with ferrous salts; no precipitate with magnesium salts. With zinc, manganese, cadmium, and silver salts, it forms precipitates which dissolve in boiling water and crystallise out on cooling. The cupric and mercuric salts are likewise soluble in hot water.

* Van't Hoff has pointed out that all compounds capable of rotating the plane of polarisation of a ray of light have one or more asymmetric atoms of carbon in their formulae; the converse does not hold good, however, that all compounds containing asymmetric carbon-atoms are optically active, but he has discussed a possible explanation of this (see art. LIGHT, section Circular Polarisation, *Theory of the Constitution of optically active bodies*).

† It may be questioned whether any two compounds different in physical characters are precisely alike in so-called chemical properties; the two tartaric acids, which probably resemble each other more closely than any other two compounds with which we are acquainted, undergo fermentation, it is said, with different degrees of readiness, the dextro-rotatory acid disappearing first.

Iso-oxycumic acid heated alone to 235° – 238° or with hydrochloric acid to 190° , is for the most part resolved, with ebullition, into carbon dioxide and the corresponding phenol, viz. *metapropylhydroxyl-benzene*, $C^6H^{11}(OH) = C^6H^4(C^3H^2)(OH)$. See PHENOLS and PROPYL-BENZENE.

ISOPENTYLMETHYL KETONE. See KETONES.

• **ISOPIANIC ACID.** See NARCOTINE-DERIVATIVES.

ISOPIC ACID, syn. with *Methylnorhemipinic acid*. See NARCOTINE-DERIVATIVES.

ISOPICRIC ACID. See PICRIC ACID.

ISORCIN. See ORCIN.

ITACONIC ACID. See PYROCITRIC ACID (p. 517).

ITADIBROMOPYROTARTARIC ACID. See PYROTARTARIC ACID.

ITAMALIC ACID and **ITATARTARIC ACID.** See PYROCITRIC ACIDS (p. 518).

IXOLYTE. A fossil resin, occurring in the lignite of Gloggnitz, in the form of fluid drops which darken in colour and harden on exposure to the air. When fused with potash, it yields pyrocatechin (Weidel, *Wien. Akad. Ber.* [2], lxxiv. 387).

J

JABORANDI. This is the native name for several drugs of a sudorific and salivating character, consisting of the leaves and twigs of various species of *Pilocarpus* and other trees growing in Brazil, Paraguay, and Pernambuco. Some varieties are said to be obtained from *P. pinnatifolius* growing in northern Brazil. According to E. M. Holmes (*Pharm. J. Trans.* [3], v. 581, 641) the jaborandi of Pernambuco is most probably obtained from *P. Selloanus*; according to Schelenz (*Arch. Pharm.* [3], vii. 414) and Baillon (*ibid.* 327) the drugs included under the name of Jaborandi are obtained from a whole series of plants belonging to different families.

Byasson (*Pharm. J. Trans.* [3], v. 826) has obtained from Jaborandi leaves an alkaloid which he calls jaborandino, and regards as the active principle of the plant. It is viscid; tastes sharp and bitter; volatilises like nicotine with vapour of water in presence of ammonia; dissolves in chloroform, ether, absolute alcohol, ammoniacal water and dilute acids.

A. W. Gerrard (*ibid.* 865, 965) prepares from jaborandi bark an alkaloid which he calls pilocarpine. The bark is exhausted with alcohol; the soft extract remaining after evaporation of the solvent is washed on a filter with water; the watery filtrate is evaporated at a gentle heat to the consistence of a fluid extract; ammonia is added in slight excess; and the liquid is shaken up with chloroform. The chloroform solution when evaporated yields impure pilocarpine. The hydrochloride, nitrate, and sulphate of this base are crystalline salts which dissolve in water and produce the characteristic physiological effects of jaborandi. Gerrard also found in jaborandi an acrid resin, tannic acid, chlorophyll and a volatile oil.

E. Hardy (*Bull. Soc. Chim.* [2], xxiv. 497) prepares pilocarpine by exhausting jaborandi leaves with water; evaporating the liquid to a syrup; mixing the residue with excess of magnesia and drying it; exhausting the dried residue with chloroform; evaporating the extract, dissolving the residue in water; and evaporating the filtered solution in a vacuum. Pilocarpine thus obtained is a syrupy mass, forming crystalline salts with hydrochloric, nitric and sulphuric acids.

By distilling jaborandi leaves with water, Hardy obtained a volatile oil consisting mainly of a hydrocarbon, $C^{10}H^{16}$, called pilocarpene, having a fragrant odour, a specific gravity of 0.852 at 18° , vapour-density = 4.0, and boiling at 178° .

Kingzett (*Chem. Soc. J.* xxxii. 367) finds that the alkaloid obtained from the stalks and branches of jaborandi is amorphous, and yields an uncrystallisable hydrochloride. The gummy base dried in a vacuum gave by analysis numbers agreeing with the formula $C^{22}H^{35}N^4O^4$, $4H_2O$, and that of the platino-chloride dried at 80° , led to the formula $C^{22}H^{35}N^4O^4$, $2HCl$, $PtCl^4$. This salt crystallises in reddish-yellow octohedrons slightly soluble in cold, easily in hot water.

On the physiological action of jaborandi, see Continho a. Gubler (*N. Rep. Pharm.*

xxiv, 231, 233; Robin, *ibid.* 236; *Jahresb. f. Chem.* 1875, 888; M. Stumpf, *N. Rep. Pharm.* xxv. 703).

JACOBSITE. A mineral from Långban belonging to the spinel group; it is strongly magnetic and has the following composition:

Fe ² O ³	Mn ² O ³	MnO	MgO	CaO	P ² O ⁵	Pb	Insol. residuc
58.39	6.96	29.93	1.68	0.40	0.06	1.22	2.17 = 100.81 %

leading to the formula $MnO(Fe^{2}O^{3}, Mn^{2}O^{3})$ (A. E. Nordenskiöld, *Jahresb. f. Min.* 1878, 206).

JAMESONITE. *Sulphantimonite of Lead* (iii. 442).—This mineral occurs, together with arsenical pyrites, iron pyrites and copper pyrites, in a vein of crystalline calcite implanted on clay-slate in the Sierra de los Angeles, the northern continuation of the Sierra de Famatina in the Argentine Republic (p. 733). It forms fibrous to cauline aggregates or crude masses; has a specific gravity of 4.25; melts without decrepitation when heated; and gives by analysis the following numbers:

S	Sb	As	Pb	Ag	Cu	Zn	Fe
21.75	32.00	0.20	39.05	1.34	3.45	0.62	2.00 = 100.41

(A. Stelzner, *Jahrb. f. Min.* 1874, 537).

JAROSITE. This native potassio-ferrous sulphate originally found in yellowish rhombohedrons at Baranco Jaroso, near the Sierra Amugnora in Spain (iii. 443), occurs also at Boresowsk, in blackish-brown crystals exhibiting the combination R. OR. Angle R : R = 89.8° (N. v. Kokscharow, *Jahrb. f. Min.* 1875, 872).

JAVANINE. An alkaloid not yet fully examined, occurring in the bark of *Cinchona Calisaya*, var. *Javanica* (Hesse, *Ber. x.* 2152).

JEFFERISITE. This name was given by Brush to a chloritic mineral from the serpentine of West Chester, Pennsylvania (vi. 763). The same mineral occurs accompanying corundum in the Culsagee mine near Franklin, Macon County, N. Carolina. *Analysis*: 1. Broadly laminar variety from the Culsagee mine, analysed by König. 2. The same by Chatard. 3. A greenish-brown-yellow microlaminar variety from the same locality analysed by Chatard. 4. Broadly laminar variety from West Chester, by König. 5. The same by Chatard:

	SiO ²	AlPO ⁴	Fe ² O ³	FeO	MgO	Loss by ignition
1.	33.93	17.38	5.42	0.50	23.43	19.17 = 99.83
2.	33.77	17.56	5.61	0.50	22.48	20.30 = 100.22
3.	34.00	20.36	4.91	0.42	21.71	18.50 = 99.90
4.	33.35	17.78	7.32	2.11	19.26	19.87 = 99.69
5.	34.40	16.63	8.00	2.11	19.30	19.03 = 99.47

Small quantities of potash and soda were also present but not determined (F. A. Genth, *Contributions from the Laboratory of the University of Pennsylvania*, No. 1. *J. pr. Chem.* [2], ix. 49).

JERVINE. See VERRATRUM ALKALOIDS.

JEYPOORITE. This, according to W. A. Ross (*Proc. Roy. Soc.* xxi. 292), is the correct name of the native cobalt sulphide, hitherto called *Synpoorite* (1.1050), occurring in the copper mines of *Khetree* in the principality of Jeypoor in Rajpootana, India. A blow-pipe analysis made with a very small quantity of material gave 82 per cent. cobalt, 7 antimony, 6 arsenic, and at most 5 sulphur, whereas the older analysis by Middleton gave 64.64 Co and 35.36 S, agreeing nearly with the formula CoS. The mineral occurs in very small monometric crystals $\infty O \infty . O . \infty O$, in an intimate sandy mixture of magnetic pyrites, copper pyrites and quartz.

JOGYNAITE. This name was given by the late N. v. Nordenskiöld to a mineral species (commonly regarded as an earthy scorodite) formed by decomposition of arsenical pyrites in the mountain-range of Adan-Tschilon, in the Government of Nertschinsk (N. v. Kokscharow, *N. Petersb. Acad. Bull.* xix. 564).

JORDANITE. This sulphur-compound, originally found in the Binnenthal (vi. 763), occurs also at Nagjag (Tschermak, *Jahrb. f. Min.* 1874, 188). *Analyses*: (1 and 2). From the Binnenthal (Sipöcz, *Jahrb. f. Min.* 1873, 614). (3). From Nagjag (E. Ludwig, *ibid.* 1874, 188):

	S	As	Sb	Pb
(1).	18.18	12.78	—	68.99 = 99.95
(2).	18.13	12.86	0.11	68.95 = 100.05
(3).	17.06	9.90	1.87	70.80 = 99.63

Sipöcz deduces from his analyses the formula $PbAs_2S_7$.

JUGLONE. See NUCIN.

JUNIPER. The following analysis of juniper-berries, differing considerably from that by Donath (vii. 710), is given by Ritthausen (*Landw. Versuchs-St.* xx. 409):

Water	10.77 per cent.	Other substances soluble	
Fat, resin and essential		in water	11.70 per cent.
Oil	12.24 "	Non-nitrogenous matter	
Albuminoids	5.41 "	sol. in H ² SO ⁴ , and in	
Woody Fibre	31.60 "	caustic alkalis, but not	
Grape-sugar	14.36 "	in water	10.55 "
		Ash	3.37 "

JUTE. The fibre of certain tiliaceous plants cultivated in Bengal, chiefly the annuals, *Corchorus capsularis* and *C. olitorius*. The sowing takes place in March or April, and the crop is reaped in August before the seeds are ripe. The plants, which grow to the height of about 12 feet, are tied up in bundles and retted in water for five or six days, and then swung in the air to separate the long fibres from the brittle woody matter. In this state the jute is imported into Europe. Successful attempts have also been made to cultivate jute in China and in America, where it is used for the packing of cotton.

The crude jute, about 12 feet long, is usually somewhat woody at the lower end. It is nearly colourless at first, but becomes dark-coloured after some time. It is bleached by passing it, first through an alkaline bath and then through a bath of magnesium or sodium hypochlorite.

Jute is easily distinguished by the microscope from flax, cotton and hemp by the very irregular thickness of its cell-walls, so that the central space does not conform to the external outline, whereas flax fibre consists of bundles of cells having thick walls and a circular outline. Jute fibre, like all woody fibres, is coloured yellowish-red by aniline sulphate, and the presence of a considerable amount of woody matter in jute is shown by the great depth of colour which it acquires when thus treated, whereas hemp is scarcely affected by the same reagent, and flax not at all.

Retted jute fibre dried at 100° C. contains 15.540 per cent. water, 83.131 organic matter and 1.329 ash. A more detailed analysis gave the following results.

Wax and fatty matters, soluble in ether	=	0.235
Tannic acid and colouring matters soluble in alcohol	=	1.135
Sugar, Pectin	=	2.427
Soluble Nitrogenised matters	=	0.512
Insoluble Nitrogenised matters	=	2.433
Inorganic matters united with fibre	=	1.010
Cellular fibre	=	92.248
		100.000
Nitrogen in original fibre	=	10.291
Nitrogen in the fibre after treatment with solvents	=	10.210

The fibre in its crude state contains 0.291 per cent. nitrogen, and after exhaustion with the reagents above mentioned, it still retains 0.210 per cent.

The quantity of jute imported through Dundee alone amounts yearly to 100,000 tons, and in addition large quantities are imported by way of London, Liverpool and Glasgow.

Jute is used for the manufacture of all kinds of coarse spun and woven fabrics, such as sacking, mats, stair-carpets, &c. It also forms an excellent material for the making of false hair, and for the substance of silk hats.

K

KAINITE. H. Schwarz (*Dingl. pol. J.* cccix. 345) has analysed two samples of crude kainite from Kalusz in Galicia (vii. 710), with the following results:

K ² SO ⁴	MgSO ⁴	NaCl	MgCl ²	Clay	Water and Loss
21.55	18.21	29.02	12.79	2.38	16.05 = 100
22.77	17.20	28.92	14.60	5.65	15.86 = 100

These numbers represent a mixture of about 51 per cent. schönite, (K^2SO^4 , $MgSO^4$, $6H^2O$), 24–29 sodium chloride, 17–19 magnesium chloride (with $2H^2O$), and 2 to 3 clay.

To obtain the potassium sulphate from this salt, Schwarz recommends the use of finely ground gypsum, which separates a double sulphate of potassium and magnesium. This double salt may be decomposed by boiling water, which dissolves out the potassium sulphate; and the residual gypsum, perhaps containing a little potash, may be utilised for the decomposition of fresh quantities of kainite.

Use of Kainite as Manure.—Experiments on the manurial effect of Stassfurt kainite (24·97 K^2SO^4 , 12·01 $MgSO^4$, 14·70 $MgCl^2$, 32·40 $NaCl$, 1·46 $CaSO^4$, 12·00 water, and 1·56 insoluble matter) have been made by P. Wagner (*Landw. Versuchs-St. Darmstadt*, 1874), leading to the following results. The potash introduced into the soil in the form of kainite, distributes itself more uniformly and more widely than pure potassium salts: consequently manuring with kainite is especially beneficial to deep-rooting plants. The chlorine-compounds in the kainite must be washed out of the soil, as they act injuriously on vegetation; and for this reason kainite must be laid upon the land in autumn, winter, or the beginning of spring. There is no fear of washing out the potassium salts at the same time. If an abundant enrichment of the soil with potash is desired, pure potassium salts are preferable to kainite.

KAISER OIL. See PETROLEUM.

KAOLIN. Analyses of several kaolins used in Austria for the manufacture of bricks are given by F. Fischer (*Dingl. pol. J.* cccxxvii. 65; *Chem. Soc. J.* xxxiv. 691). The composition and properties of kaolin from the Middle Variegated Sandstone of Thuringia are described by H. Harold (*Jahrb. f. Min.* 1875, 877; *Chem. Soc. J.* xxix. 530) and by E. Schmid (*Jahrb. f. Min.* 1876, 669; *Chem. Soc. J.* xxxii. 119). A silicate having the composition of kaolin, $Si^2Al^2H^4O^8$, but differing from it in specific gravity, and other physical properties, occurs imbedded in the porphyry of Stein in Carniola. Sp. gr. = 2·209. Analysis:

SiO^2	Al^2O^3	CaO	MgO	H^2O	
45·97	38·96	1·17	0·12	14·24	= 100·46

(F. Ullik, *Min. Mitth.* 1873, 197).

Kaolin from Göppersdorff, in the circle of Strehlon, Silesia, contains, according to C. Bischof (*Dingl. pol. J.* cccxiii. 60).

SiO^2 (C)	SiO^2 (V)	Al^2O^3	MgO	CaO	Fe^2O^3	K^2O	Na^2O	Loss by ignition	
21·44	49·00	21·35	trace	0·23	0·61	0·84	0·68	7·08	= 100·23.

A kaolin from Langenstriegis near Freiberg contains, according to A. Frenzel (*Jahrb. f. Min.* 1874, 675), 48·82 per cent. SiO^2 , 38·51 Al^2O^3 , and 13·20 H^2O (= 100·53). Under the microscope this kaolin appears to consist of crystalline granules.

A plastic material from Collonges, near Fort l'Ecluse in the Department of Ain, differing from kaolin by its smaller amount of silica and larger amount of water, has been analysed by Ador a. Rilliet (*N. Arch. ph. nat.* xlix. 242). By decomposition with sodium carbonate it was found to contain 38·22 per cent. SiO^2 , and 35·40 Al^2O^3 ; with strong hydrochloric acid it yielded 39·60 SiO^2 and 34·01 Al^2O^3 .

On the separation of kaolins by levigation, see Schlesing, p. 552 of this volume; also *Jahresb. f. Chem.* 1874, p. 1261.

KAPOK. The kapok-tree (*Eriodendron anfructuosum*) of Java and the Indian Archipelago, bears a seed resembling, in many respects, that of the cotton-plant. Like cotton-seed, it is covered with a wool, which, though less suited for spinning than cotton, has long been used in India and the Netherlands for filling bolsters, &c.

The following analyses show the composition of a trial-cake made from this seed, as compared with that made from seed of the cotton-plant:—

	Kapok cake	Cotton cake
Water	13·28	12·60
Nitrogenous (albuminous) compounds	26·34	20·62
Fat	5·82	6·36
Non-nitrogenous extractive matter	19·92	35·42
Woody fibre	28·12	20·36
Ash	6·52	5·64

The ash of the seed contains 28·5 per cent phosphoric acid and 24·6 per cent. potash; it would, consequently, have about the same manurial value as linseed (Reinders, *Landw. Versuchs-St.* xix. 161).

KARARFVEITE. A mineral containing fluorine, from Kararfvet, near Fahlun in Sweden, formerly mistaken for gadolinite. It occurs in light yellow to brown imperfect crystals and crystalline masses, sometimes weighing more than a kilogram, and associated with gadolinite and hjelmito. Sp. gr. 4·93. Analyses made with very impure material gave, as a mean result:

Oxides of Ce, La, Di	CaO	MgO	Fe ² O ³	P ² O ⁵	F	H ² O
67·40	1·24	trace	0·32	27·38	4·35	traco = 100·69

(F. Radominski, *Compt. rend.* lxxviii. 764).

KAURI GUM. Syn. with DAMMARA RESIN (p. 625).

KAIVA-ROOT. The root of *Piper methysticum* (iii. 455). E. Nölting & A. Kopp (*Monit. scient.* [3], iv. 9, 20) have found, in the alcoholic extract of this root, besides kawain—which is not a glucoside—a body, likewise neutral and free from nitrogen, crystallising in prismatic needles, and like kawain yielding benzoic acid by oxidation. Kawain agrees in many of its properties with cubebin, but differs from it in the composition of its nitro-derivatives.

According to Cuzent (*Analyst*, i. 150; *Jahresb. f. Chem.* 1876, 894), kawain, karakin, or methysticin is insoluble in water, and is coloured red by hydrochloric acid, the colour changing to a splendid yellow on exposure to the air. Strong sulphuric acid colours kawain purple-violet, changing to green.

KEATINGIN. A mineral resembling Fowlesite (v. 107), occurring in a mass of yellow garnet at Franklin, New Jersey. The angles of its cleavage-prism measure 64° and 116°. Sp. gr. = 3·33. Composition:

SiO ²	MnO	ZnO	CaO	H ² O
47·8	27·7	5·6	18·0	0·8 = 99·9

(C. U. Shephard, *Sill. Am. J.* [3], xii. 231).

KENNGOTTITE. See MIARGYRITE.

KERAMOHALITE. This hydrated aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, originally found near Königsberg in Hungary (ii. 446), occurs also as a granular, crystalline, ochre-yellow efflorescence, on the clay-substance interposed between the lignite beds of the Bauersberg near Bischoffsheim, Rhön. The mineral from this latter locality gave by analysis 16·7 per cent. Al_2O_3 , 4·2 Fe_2O_3 , 2·9 FeO, 2·3 MgO, 39·3 SO_3 , and 33·3 H_2O (= 98·7) (A. Hilger, *Jahrb. f. Min.* 1877, 420).

KEROSIN. See PETROLEUM.

KERRITE. A mineral accompanying corundum in the Culsagee Mine, North Carolina. See CORUNDUM (p. 570).

KERSANTITE and **KERSANTON.** These names are applied to certain dioritic rocks occurring in granite and in the oldest sedimentary formations, in the Vosges and in the roadstead of Brest. 1. *Kersantite* from Visembach in the Vosges, where it forms an irregular vein in a gneiss-granite, consists for the most part of 70 per cent. oligoclase and 30 per cent. mica, sometimes together with hornblende, and is almost wholly crystalline. It lost by ignition 1·93 per cent., consisting essentially of water, carbon dioxide, and organic matter. 2. *Kersantite* from Sainte-Marie aux Mines, forming a vein in a syenite-granite, differs from the preceding by its less decided crystalline structure. Loss by ignition 1·70 per cent. 3. *Kersantite* (also called *Kersanton*) from Brest, is very much like the two preceding. It often has a granitic structure, and contains triclinic felspar exhibiting the usual twin-striation; mica of a pinchbeck-brown, brown-black or black colour, and a magnesium-iron mica; dark-green iron-spar, somewhat resembling hornblende; white or red calcite, filling up the interstices between the felspar, and occurring also in veins. Kersanton includes in its mass iron pyrites and a large quantity of magnetic pyrites, microscopic grains of magnetic iron oxide, very rarely quartz, sometimes epidote in thin irregular veins. A green hydrated silicate of iron and magnesium (*Chlorite ferrugineux*) is likewise found, especially in the cavities. The loss by ignition (chiefly CO_2) was found in three specimens to be 4·49, 6·75, and 7·41 per cent. The analysis of a Kersanton from Daoulas, commonly used for building in Brest, and effervescing strongly with acids, gave:

SiO ²	Al_2O_3 , FeO, MgO, K ² O, Na ² O	Cr ² O ³	CaO	CO_2, H_2O
52·80	35·05	traces	5·40	6·75 = 100

(Delesse, *Bull. Géol.* [2], vii. 704; *Jahresb. f. Chem.* 1850, 802).

4. *Kersantite* from Langonschwalbach, Nassau, has been analysed by E. Zicken-drath (*Jahrb. f. Min.* 1875, 753). Like the rocks above described, it is a mixture of

oligoclase and mica in varying proportions. Where the mica predominates, the rock appears compact, with the dark brownish-black colour of triclinic felspar; the mass is coarse-grained and lighter in colour. The oligoclase has a reddish-white to pure white colour, and with a lens the twin-striation is perfectly distinct. The mica crystallises in the rhombic system, and has a brownish-black colour, which, however, appears brownish-yellow in thin laminae. Augite occurs nearly always in this rock, but generally partially decomposed, with the original form still recognisable. Magnetite occurs in grains, apatite in colourless needles. Iron-pyrites is distributed in small crystals throughout the whole mass, which is also strongly impregnated with carbonates. Quartz is also observed, but is difficult to recognise. Oligoclase, quartz, iron-pyrites, and carbonates occur, sometimes in isolated crystals; also a green mineral resembling melanolite.

Analyses.—1. Compact from Adolfsack, specific gravity = 2.75. 2. Coarse-grained from Heimbach, specific gravity = 2.86. 3. Oligoclase from the Heimbach rock, specific gravity = 2.66. 4. Mica from the Adolfsack rock, specific gravity = 2.92.

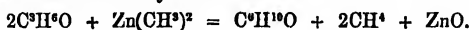
	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	MgO	CaO	K ^a O	Na ^a O	H ^a O	F	CO ^a	P ^a O ^a
1.	54.94	7.69	9.58	4.37	1.53	3.03	5.11	4.03	2.47	1.49	0.22	4.32	0.91 = 99.79
2.	53.16	7.96	9.24	4.77	1.23	3.05	6.64	3.06	2.97	1.77	0.04	4.08	1.20 = 99.17
3.	63.40	20.87	trace	—	—	trace	2.87	3.48	7.55	0.85	—	—	= 99.02
4.	40.80	11.89	18.97	—	—	11.94	3.68	10.63	—	0.55	1.05	—	= 99.51

From these data Zickendrath calculates the mineral constitution of the rock as follows:

	Adolfsack	Heimbach
Oligoclase	32.17	37.61
Mica	27.10	15.88
Iron-pyrites	0.167	0.32
Augite pseudomorphs	10.09	14.19
Apatite	1.98	2.62
Magnetite	2.74	4.5
Carbonates	9.82	9.52
Quartz	18.74	14.67
	<hr/> 102.807	<hr/> 99.31

KETONES. 1. FATTY KETONES. *Bye-products formed in the Preparation.*—

In the preparation of ketones by the action of acid chlorides on organo-zinc compounds according to the general equation, $2(R.CO.Cl) + ZnR^2 = ZnCl^2 + 2(R.CO.R)$, condensation-products are also formed by the further action of the organo-zinc compounds on the ketones. Thus, for instance, mesityl oxide, $C^6H^6O = 2C^3H^3O - H^2O$, is formed by the action of zinc-methyl on acetone:



In like manner propionyl chloride and zinc-methyl yield, besides methyl-ethyl ketone, C^4H^8O , a body having the composition $C^6H^{10}O = 2C^3H^3O - H^2O$. This compound is a colourless liquid, insoluble in water, having a density of 0.877 at 0°, 0.862 at 18°, and boiling at 167°–168°. Similarly the compound, $C^{10}H^{18}O = 2C^5H^9O - H^2O$, is formed by the action of zinc-methyl on isobutyryl chloride. It is a colourless liquid of peculiar odour, insoluble in water, boiling at 189°–191°. Sp. gr. 0.87 at 0°; 0.855 at 20°. It combines with hydrogen chloride to form a yellowish oily body ($C^{10}H^{18}ClO$) having the odour of turpentine; and with hydrogen iodide to form a dark coloured crystalline body. Lastly, a bye-product having the formula $C^{12}H^{22}O$ is formed in the preparation of dimethyl-isobutyl carbinol by the action of zinc methyl on valeryl chloride. It is a colourless liquid, insoluble in water, boiling at 217°–219°. Sp. gr. 0.864 at 0°; 0.849 at 20°. Like the two preceding bodies, it combines with hydrogen chloride and iodide.

All these compounds combine with bromine, and may, therefore, be regarded as non-saturated ketones. Their chemical structure has not yet been made out (Pawloff, *Liebig's Annalen*, clxxxvii. 104).

Oxidation.—An investigation by M. Hercz (*Liebig's Annalen*, clxxxvi. 257) of the action of various oxidising agents (potassium dichromate and sulphuric acid, chromic acid, potassium permanganate in neutral, acid, and alkaline solution, silver oxide and bromine, lead dioxide and nitric acid), on certain ketones of the fatty group (dimethyl-ketone, methyl-propyl-ketone, butyrene, caprone, and palmitone) has led to the following conclusions:

(1). Popoff's law (vi. 765; vii. 711), according to which the lower of the two alcohol-radicles in the ketone remains united with the carbonyl, and by taking up

an OH-group, is converted into a fatty acid, while the higher radicle is oxidised and forms a second fatty acid,—holds good for the ketones of normal fatty acids. (2). Whatever may be the oxidising agent used, and in whatever proportion to the ketone, a further oxidation of the primary products invariably takes place, resulting in the formation of less highly carbonised fatty acids, and ultimately of carbonic acid. (3). The oxidation is more difficult and less complete in proportion as the ketone is more highly carbonised. Palmitone, for example, is very difficult to oxidise, and yields but a small amount of normal products.

Dimethyl Ketone, Acetone, $\text{CO}(\text{CH}_3)_2$. *Action of Potash* (Hointz, *Liebig's Annalen*, clxix. 114).—When pure acetone is treated with potash-ley of sp. gr. 1.25–1.30, and then freed from the adhering alkaline liquid by a few drops of sulphuric acid, it is found to be altered in such a manner that it no longer distils completely at the heat of the water-bath, but leaves a considerable residue, which partly passes over at about 130° , as a very mobile liquid insoluble in water, partly at a temperature above 200° . The latter and thicker portion is probably phorone; the former, which after repeated fractionation boils between 130° and 132° , is probably a mixture of mesityl oxide with a more highly oxygenised body of similar boiling point. An impure commercial acetone, after treatment with potash as above, yielded, at about 170° , a distillate which after purification boiled at 166° – 168° , and had the percentage composition of acetone. This substance, which may be called *Polyacetone*, is probably analogous in constitution to the 'duplosulphacetone' described by Wislicenus (vii. 12). It is a colourless thin syrup, wholly soluble in water. Hointz supposes that it did not exist ready formed in the commercial acetone, but was formed by the action of the potash on some impurity contained therein.

Bromacetones.—On Monobromacetone, see p. 22 of this volume. On Pentabromacetone, the so-called Bromoxaform, see p. 351.

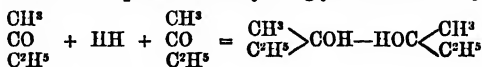
Chloracetones.—According to Theegarten (*Berl. Ber.* vi. 897) unsymmetrical dichloracetone, $\text{CH}_3\text{CO}\cdot\text{CHCl}_2$, prepared according to Mulder's directions (vii. 14), has a density of 1.326 at 0° , and forms crystalline compounds, with acid sulphites of alkali-metal.

On the Polymerides of Dichloracetone, see p. 24.

Chlorobromacetone, $\text{C}^2\text{H}^4\text{ClBrO}$ (probably $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$), is obtained by the action of hydrobromic acid on epichlorhydrin, and oxidation of the resulting chlorobromhydrin. On cooling the portion of the product which boils between 176° and 188° with ice, the chlorobromacetone separates in crystals which may be purified by recrystallisation from ether. Chlorobromacetone forms well-defined crystals melting at 34° – 35.5° , boiling at 177° – 180° , sparingly soluble in water, easily in alcohol and in ether. It has an extremely pungent odour. With sodium-hydrogen sulphite it forms a compound which resembles the corresponding compound of symmetrical dichloracetone in all respects except its crystalline form (Theegarten, *Dent. Chem. Ges. Ber.* vi. 1276).

Allyl-acetone or Methyl-crotonyl Ketone, $\text{C}^5\text{H}^{10}\text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{C}^4\text{H}^7$ (p. 14), treated with sodium in an ethereal solution floating on water, is converted into the alcohol $\text{C}^5\text{H}^{12}\text{O}$, which has a density of 1.842 at 16.2° , boils at 138° – 139° , and yields with bromine an uncrystallisable mass having the composition $\text{C}^6\text{H}^{12}\text{Br}_2\text{O}$. The acetic ether boils at 143° – 149° (J. K. Crow, *Chem. News*, xxxvi. 264).

Methyl-ethyl Ketone, $\text{C}^4\text{H}^{10}\text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{C}^2\text{H}_5$, formed by the action of zinc-ethyl on acetyl chloride, is converted by the action of sodium in presence of strong potash-ley, into the 8-carbon pinacone or octylene glycol, $\text{C}^8\text{H}^{18}\text{O}_2$.



(Lawrenowitsch, *Ber.* vii. 767).

Methyl-propyl Ketone, $\text{C}^6\text{H}^{12}\text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{CH}_2\text{CH}_3$ (b. p. 99° – 105°), is converted by sodium-amalgam and water into methyl-propyl-carbinol, $\text{C}^6\text{H}^{12}\text{O} = \text{CH}_3\cdot\text{CHOH}\cdot\text{CH}_2\text{CH}_2\text{CH}_3$, boiling at 118.5° – 119.5° (corr.) (Belohoubek, *Wien. Akad. Ber.* [2 Abth.], lxxiv. 80).

Methyl-isopropyl Ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)_2$, (b. p. 93.5°), obtained by dry distillation of a mixture of equivalent quantities of isobutyrate and acetate of calcium, is a colourless liquid, of not unpleasant odour. Sp. gr. 0.811 at 15° . It forms a crystalline compound with sodium-hydrogen sulphite, but does not reduce an ammoniacal silver solution. By oxidising agents it is converted into acetic and carbonic acids; by nascent hydrogen into a secondary pentyl alcohol (R. Münch, *Ber.* vii. 1370). Frankland & Duppa obtained the same ketone by the action of boiling

potash-ley on ethylic acetodimethylacetate (Wanklyn's isobutyrate of acetylated ethyl, vi. 768).

Chlormethyl-isopropyl Ketone, $\text{C}^3\text{H}^3\text{ClO} = \text{CH}^2\text{Cl}.\text{CO}.\text{CH}(\text{CH}^3)^2$, (inappropriately called *Chlorinated Methylisobutyl Ketone*).—This compound, formed by the action of chromyl chloride, CrO_2Cl_2 , on petroleum pentane and on inactive amyl chloride, is a colourless liquid having a pungent aromatic odour and boiling without decomposition at about 120° . It is insoluble in water and in aqueous potash; reduces ammoniacal silver solution; does not unite with bisulphites (Etard, *Compt. rend.* lxxxiv. 127).

A compound, $\text{C}^6\text{H}^{11}\text{ClO}$, probably homologous with the preceding, is formed in like manner from hexane. It easily reduces an ammoniacal silver solution, does not unite with NaHSO_3 , and is not attacked by potash. A similar body is also formed from heptane (Etard).

Methyl-butyl Ketone, $\text{C}^6\text{H}^{12}\text{O} = \text{CH}^3.\text{CO}.\text{CH}^2(\text{CH}^3)^2$, is formed by oxidation of the secondary hexyl alcohol, $(\text{CH}^3.\text{CHOH}.\text{C}^4\text{H}^9)$, obtained from petroleum hexane (p. 1030). It has a specific gravity of 0.829 at 0° , boils at 127° , and is converted by oxidation into acetic and normal butyric acids (Schorlemmer, *Liebig's Annalen*, clxi. 263).

Methyl-isobutyl Ketone, $\text{CH}^3.\text{CO}.\text{CH}^2\text{CH}(\text{CH}^3)^2$, formed by the action of zinc-methyl on valeryl chloride, has a sp. gr. of 0.819 at 0° , boils at 114° , and is converted by oxidation into acetic and isobutyric acids.

Methyl-katabutyl Ketone or Pinacolin, $\text{CH}^3.\text{CO}.\text{C}(\text{CH}^3)^3$, is formed by the action of zinc-methyl on trimethyl-acetyl chloride. As thus prepared it has the same peppermint odour as pinacolin prepared by dehydration of acetone (iv. 617) and agrees very closely with the latter in boiling point and density, as shown by the following numbers.

	Synthetical Pinacolin	Pinacolin from Acetone
Boiling point	$105.5-106.5^\circ$	105°
Sp. gr. at 0°	0.830	0.823
" " 50° "	0.791	0.787
Expansion for 1° between 0° and 50°	0.00122	0.00117

Both unite with sodium-hydrogen sulphite, and are converted by oxidation into trimethylacetic acid (Butlerow, *Liebig's Annalen*, clxxiv. 125).

Homologues of Pinacolin.—Three of these bodies have been prepared synthetically by Wischnegradsky (*Liebig's Annalen*, clxxviii. 103) by processes similar to that just mentioned for the preparation of pinacolin itself, viz. by the action of trimethyl-acetyl chloride on zinc-ethyl, and of ethyl-dimethyl-acetyl chloride, $\text{C}(\text{CH}^3)_2(\text{C}^2\text{H}^5).\text{CO}.\text{Cl}$, on zinc-methyl and zinc-ethyl respectively. The composition and principal properties of the three products are given in the following table:

	Ethyl-butyl Pinacolin $(\text{CH}^3)_2\text{C}.\text{CO}.\text{C}^2\text{H}^5$	Methyl-amyl Pinacolin $(\text{CH}^3)_2(\text{C}^2\text{H}^5).\text{C}.\text{CO}.\text{CH}^3$	Ethyl-amyl Pinacolin $(\text{CH}^3)_2(\text{C}^2\text{H}^5).\text{C}.\text{CO}.\text{C}^2\text{H}^5$
Boiling point	125.5° to 126°	131.5° to 132.5°	150.5° to 151.5°
Sp. gr. at 0°	0.831	0.842	0.845
" " 21°	0.810	0.825	0.820
Expansion coefficient from 0° to 21°	0.00109	0.00102	0.00098
Product of Oxidation	Trimethyl- acetic acid.	Ethyl-dimethyl-acetic acid.	

Hence it appears that in the oxidation of these bodies the carbonyl remains attached to the tertiary radicle, which therefore behaves in these reactions like a radicle of the aromatic group.

Dipropyl Ketone or Butyrone, $\text{C}^7\text{H}^{14}\text{O} = \text{C}^3\text{H}^7.\text{CO}.\text{C}^3\text{H}^7$, is almost the sole product of the dry distillation of normal calcium butyrate. It boils at $143^\circ-145^\circ$, yields with phosphorus pentachloride the bodies $\text{C}^7\text{H}^{14}\text{Cl}^2$ (b. p. 181°) and $\text{C}^7\text{H}^{13}\text{Cl}$ (b. p. 141°), and is converted by phosphoric anhydride into a liquid of variable boiling point. The portion which distils between 200° and 250° has the composition C^7H^{12} , and probably consists of polymerides (Tawildarow, *Deut. Chem. Ges. Ber.* ix. 1442).

Di-isopropyl Ketone, $\text{CH}(\text{CH}^3)^2.\text{CO}.\text{CH}(\text{CH}^3)^2$, prepared by dry distillation of calcium isobutyrate, and purified by repeated fractional distillation, is a colourless mobile liquid, having a strong ethereal camphorous odour, nearly insoluble in water, but dissolving in all proportions in alcohol and ether. Sp. gr. = 0.8254 at 17° . Boiling point $124^\circ-125^\circ$. It does not unite with acid sulphites of alkali-metal, but reduces an ammoniacal silver solution. By oxidation it yields isobutyric, acetic and carbonic acids, and by reduction (with sodium in a benzene solution of the ketone

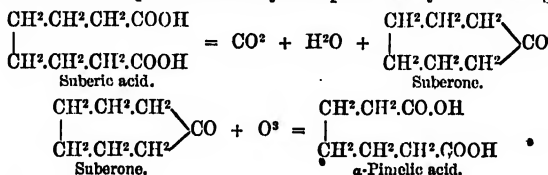
floating on water), a secondary heptyl alcohol, together with oily products of high boiling point (Popoff, *Deut. Chem. Ges. Ber.* vi. 1255; R. Münch, *ibid.* vii. 1370).

Palmitone or Dipentadecyl Ketone, $C^{31}H^{62}O = C^{15}H^{31}.CO.C^{15}H^{31}$. This ketone, subjected in the fused state to the action of bromine, is converted into a yellowish oil, which after purification solidifies in a freezing mixture and melts at 5.6° . Its analysis gave results which might be represented either by the formula $C^{31}H^{60}Br^2O$ (tribromopalmitone hydrobromide), or by $C^{31}H^{61}Br^2O$ (dibromopalmitone hydrobromide). The latter is perhaps the more probable, as, under similar conditions, a body was once obtained which crystallised from ether in white laminae containing an amount of bromine which agreed with the formula of dibromopalmitone (Hercz, *Liebig's Annalen*, cxxxvi. 257).

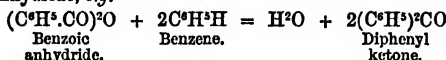
On the Oxidation of Palmitone, see p. 1147.

Suberone, $C^8H^{14}O$. The constitution of this body, hitherto somewhat doubtful (v. 450), has been determined by Schorlemmer and R. S. Dale (*Chem. Soc. J.* xxvii. 935). The crude product of the distillation of suberic acid with lime yields on fractionation, first a small quantity of hexane, and then a distillate from which pure suberone is easily separated by fractional distillation, a tarry mass remaining behind.

Suberone is a colourless liquid having a pungent odour, like that of peppermint, and boiling at 179° – 181° (mercury-column wholly in the vapour). By strong nitric acid it is oxidised to α -pinelic acid (*q. v.*) Regarding suberic acid as a normal compound, i.e. as having all its carbon-atoms in a single chain, the formation and constitution of suberone and α -pinelic acid may be represented by the following equations:

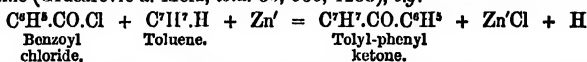


II. AROMATIC KETONES. *Formation*.—1. By heating aromatic hydrocarbons with mixtures of benzoic acid and its homologues, or the corresponding anhydrides, and phosphoric anhydride, *e.g.*



(Kollarits a. Merz, *Deut. Chem. Ges. Ber.* vi. 446, 536).

2. By heating aromatic hydrocarbons with acid chlorides, in presence of finely divided zinc (Grucarevic a. Merz, *ibid.* 60, 966, 1238), *e.g.*



3. By the action of aluminium chloride on a mixture of an acid chloride and a hydrocarbon (Friedel, Crafts a. Ador, *Compt. rend.* lxxxv. 672), *e.g.*



also by the action of carbonyl chloride on a hydrocarbon in presence of aluminium chloride, an acid chloride being first formed (*e.g.* $C^6H^6 + \text{COCl}^2 = \text{HCl} + C^6H^5.CO.Cl$), which then reacts with the hydrocarbon and the aluminium chloride as above.

Phenyl-methyl Ketone or Acetophenone, $C^8H^8O = C^6H^5.CO.CH^3$. This compound, treated with sodium-amalgam, yields: (1). The pinacone of acetophenone, $C^6H^5.C(OH).CH^3$

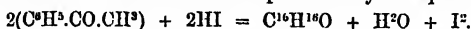
or phenyl-methyl glycol, $C^6H^5.C(OH).CH^3$, which separates from dilute ethyl alcohol

in spicular crystals, and from the secondary alcohol formed at the same time, in crystals belonging to the quadratic system. (2). Phenyl-methyl Carbinol, Secondary Ethyl-benzene Alcohol, or Secondary Acetophenonic Alcohol, $C^6H^5.CHOH.CH^3$, contained in the portion of the crude product which passes over between 190° and 210° . This last compound is a colourless, strongly refracting, fetid liquid, having a density of 1.013, and boiling at 202° – 203° (Emmerling and Engler, *Ber.* vi. 1005). See PHENYL ALCOHOLS.

On the action of dry ammonia and phosphoric anhydride on acetophenone, whereby triphenyl-benzene, $C^6H^5(C^6H^5)^3$, and the so-called acetophenonine, $C^{24}H^{18}N$ or $C^{24}H^{20}N^2$, are produced, see vii. 940.

When acetophenone (20 grams) is heated to 130° – 150° with hydriodic acid

(10–15 grams) and phosphorus (1.8 grams), for eight to ten hours, part of the phosphorus remains unattacked, and the chief product of the reaction is an oxygenised body, C^6H^5O , which may be obtained pure by recrystallising the portion of the product which distils over at 300° – 340° , after freeing it from iodine and phosphorus. This compound crystallises in white laminae or transparent colourless plates, melts at 70° , and boils at 340° – 345° (mercury column wholly in the vapour); it is insoluble in water, but dissolves very easily in ether, carbon sulphide, benzene, and hot alcohol, less easily in cold alcohol. Its formation is represented by the equation:



It is related to acetophenone in the same manner as pinacolin to acetone, but its constitution is probably not analogous to that of pinacolin, but rather that which is represented by the formula $C^6H^5.CO.CH^2.CH \begin{smallmatrix} < C^6H^5 \\ < CH^3 \end{smallmatrix}$, according to which it may be supposed to be produced by hydrogenation of a previously formed condensation product, $C^6H^5.CO.CH=C \begin{smallmatrix} < C^6H^5 \\ < CH^3 \end{smallmatrix}$. By further hydrogenation it is converted into

diphenyl-dimethylethane, $C^6H^5.CH.CH^3$, which is also produced directly by

heating acetophenone with hydriodic acid and phosphorus; and by the action of sodium on phenylmethyl-carbinyl bromide, $C^6H^5.CHBr.CH^3$, or the corresponding chloride (Graebe, *Deut. Chem. Ges. Ber.* vii. 1623).

Substitution-derivatives of Acetophenone.

Acetophenone can yield two series of substitution-derivatives, according as the substituted radicle enters into the phenyl or the methyl group. There is great confusion in the nomenclature of these derivatives, but they are best designated by names which indicate directly the positions of the substituted radicles, e.g.

$C^6H^4Cl.CO.CH^3$
Chlorophenyl-methyl Ketone
or Acetochlorophenone.

$C^6H^5.CO.CH^2Cl$
Phenyl-chloromethyl Ketone
or Chloracetophenone.

Brominated Acetophenones (Emmerling a. Engler, *Ber.* iv. 148; Hunnius, *ibid.* x. 2006).—According to Emmerling a. Engler, two modifications of this compound are formed simultaneously by the action of 2 atoms of bromine on 1 mol. acetophenone at ordinary temperatures; and, on treating the product with dilute alcohol, acetobromophenone, $C^6H^4Br.CO.CH^3$, is dissolved, while bromacetophenone, $C^6H^5.CO.CH^2Br$, remains in the form of a syrupy mass, which solidifies only after a considerable time. Acetobromophenone separates from solution in dilute alcohol by slow evaporation in colourless laminar crystals melting at 50° . It has a pungent odour, and exerts a violent irritating action on the eyes. It dissolves easily in alcohol and ether, but is insoluble in water, which moreover does not attack it sensibly even at the boiling heat. By oxidation with chromic acid mixture it is converted into bromobenzoic acid, whereas bromacetophenone, $C^6H^5.CO.CH^2Br$, yields, by oxidation with the same reagent, bromine and benzoic acid.

Hunnius, on the other hand, by dropping 1 mol. bromine into a solution of 1 mol. acetophenone in carbon sulphide, obtained nothing but bromacetophenone (which he designates as *acetophenone bromide*), exhibiting the crystalline form, melting point, and solubility ascribed by Emmerling and Engler to acetobromophenone, but converted by oxidation with permanganate into benzoic acid.

Bromacetophenone or *Nitrophenyl-bromomethyl Ketone*, $C^6H^4NO_2.CO.CH^2Br$, is obtained by slowly adding bromacetophenone to fuming nitric acid in a cooled vessel; when separated by water, washed with sodium carbonate, and crystallised from dilute alcohol, it forms small needles melting at 96° , soluble in alcohol, chloroform, and carbon sulphide, very slightly soluble in ether, insoluble in water. By oxidation it yields metanitrobenzoic acid; by reduction with tin and hydrochloric acid it is converted into acetamidophenone or amidophenyl-methyl ketone, the hydrochloride of which, $C^6H^4NH^2.CO.CH^3.HCl$, forms easily soluble colourless needles, turning brown on exposure to air and light.

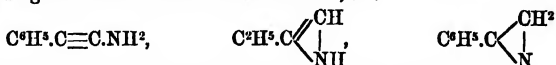
Bromacetophenone treated with potassium acetate and ethyl alcohol, or with silver benzoate and toluene, yields the compounds $C^6H^5.CO.CH^2(OC^2H^5O)$ and $C^6H^5.CO.CH^2(OC^2H^3O)$, which are respectively the acetic and benzoic ethers of benzoyl carbinol, or primary acetophenonic alcohol, $C^6H^5.CO.CH^2OH$ (Hunnius). See PHENYL ALCOHOLS.

Dibromacetophenone or *Phenyl-dibromomethyl Ketone*, $C^6H^5.CO.CHBr^2$, obtained similarly to the monobrominated compound, with 2 mols. bromine to 1 mol. acetophenone, melts at 36° , is insoluble in water, but dissolves in almost all other solvents, and crystallises with great facility. By potassium permanganate it is converted into benzoic acid; by solution of sodium carbonate, apparently into benzoyl-formic acid, $C^6H^5.CO.COOH$. With alcohol and potassium acetate it yields an oil which solidifies in a vacuum, and probably consists of the other, $C^6H^5.CO.CH(C^6H^5O)^2$.

Phenyl-chloroacetyl Ketone, *Chloracetophenone*, or *Chloroacetyl-benzene*, $C^6H^5.CO.CH^2Cl$.—To prepare this compound, chlorine is passed into the vapour of boiling acetophenone in quantity equal to that which can be evolved by the use of a quantity of manganese dioxide equal in weight to the acetophenone; the product is then distilled, and the liquid which passes over below 200° is again subjected to the same treatment. The crude product is best purified by crystallising it in a freezing mixture and drawing away the portion which liquefies at ordinary temperatures.

Pure chloracetophenone is colourless, permanent in the air, very soluble in alcohol, ether, and benzene, insoluble in water. It melts at 58° – 59° , and boils without decomposition at 244° – 245° (uncorr.) It has a pleasant aromatic taste, but its vapour excites a flow of tears. From the fused state as well as from its alcoholic solution, it separates in large well-defined crystals. The crystals separated from alcoholic solution were found by Friedlander to belong to the orthorhombic system. Axes $a : b : c = 0.9957 : 1 : 0.2135$. Observed forms ∞P_∞ , ∞P , P_∞ , $2P_\infty$. Tabular development parallel to a . Angle $\infty P : \infty P = 89^\circ 46'$; $P_\infty : P_\infty = 24^\circ 12'$. Plane of optic axes the brachypinacoid ∞P_∞ . Axis a the first median line. Angle of optic axes in oil about 74° (Staedel).

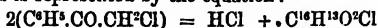
Action of Ammonia.—When chloracetophenone is boiled with aqueous ammonia for about an hour, or heated with it in a sealed tube to 140° – 150° , it is converted into a deep-red liquid which solidifies on cooling, while the whole of the chlorine remains as sal-ammoniac in the aqueous solution. From this red product two compounds may be isolated by means of ether, one remaining undissolved when the crude product is heated with ether for a short time, the other separating slowly from the red ethereal solution. The former, which is produced in small quantity only, is an isomeride of indole, C^8H^7N (Staedel a. Rugheimer, *Ber.* ix. 563, 798, 1758). For the properties of this iso-indole, see p. 1089. Staedel (*ibid.* x. 1830) points out that of the three following formulæ by which it might be represented, supposing its molecular weight to be the same as that of indole, viz.



the last seems to be the most probable, on account of the stability of iso-indole towards acetic acid at 150° , acetic anhydride at 130° – 140° , acetyl chloride at 120° , and ethyl iodide at 100° , also (which affords an argument against the double carbon-linking) towards fuming hydrobromic acid at 130° – 140° , fused potash, and faintly-glowing quicklime.

The second product of the action of ammonia on chloroacetyl-benzene is formed most abundantly when alcoholic ammonia is used. It is free from nitrogen; crystallises in long prisms or needles; is insoluble in water, alcohol, ether, benzene, carbon sulphide and acetone; and melts at 89° . It dissolves in strong hydrochloric acid, and is reprecipitated by water.

When dry ammonia gas is passed at intervals of ten to twelve hours through a cooled ethereal solution of chloracetophenone till the liquid is saturated, crystals of sal-ammoniac separate abundantly after five or six days, and the product contains, besides these and a trace of red resinous substance, two isomeric bodies having the formula $C^6H^5O^2Cl$. One of these bodies is moderately soluble in alcohol and ether, and crystallises therefrom in stellate or moss-like groups of needles; it melts at 117° , sublimes undecomposed and is easily oxidised to benzoic acid. The other isomeride is less soluble in alcohol and ether, crystallises in isolated prisms, melts at 155° , sublimes undecomposed, and is less easily oxidised than the preceding. The formation of the two bodies is represented by the equation:



(Staedel a. Rugheimer).

Phenethenyl-methyl Ketone or *Acetocinnamone*, $C^6H^5O = C^6H^5.CH=CH.CO.CH^3$ (Engler a. Leist, *Berl. Ber.* vi. 254). This ketone is prepared by the dry distillation of a mixture of the calcium cinnamate and acetate. On fractionating the first portions of the oily distillate (35 per cent. of the calcium cinnamate) the acetocinnamone passes over between 220° and 270° . It is a fragrant

liquid having a density of 1.008 and boiling at 240° – 241° ; unites with bisulphites, forming crystalline compounds, from which it is separated in the pure state by sulphuric acid; gives by nitration and subsequent oxidation, para- and meta-nitrobenzoic acids, and is converted by nascent hydrogen into phenethyl-methyl carbinol, $C^{10}H^{14}O = C^6H^5.CH^2.CH^2.CH(OH).CH^3$ (also called *pseudobutyl-benzene alcohol*), which melts at 68° , and is metameric with thymol, cymphenol and cymyl alcohol.

The portions of the distillate obtained by heating the mixture of calcium acetate and cinnamate, which boil below 220° , contain benzene, toluene, a hydrocarbon having the composition C^8H^8 or $C^{10}H^{12}$, and cinnamene; the portions collected between 290° and 330° contain a hydrocarbon C^8H^8 melting at 117° (probably a polycinnamene) which gradually separates from the distillate in plates. The portion which goes over above 330° contains a body, $C^{20}H^{18}O$ (perhaps the acetocinnamic analogue of mesityl oxide). The true ketone of cinnamic acid was not found in either of these distillates; neither was it obtained by distilling calcium cinnamate alone—a process which yields a large quantity of a compound apparently consisting of a polycinnamene.

The following methods of preparing acetocinnamone were also tested by Engler a. Leist (*Deut. Chem. Ges. Ber.* vi. 257). The sodium-derivative of cinnamic aldehyde was heated with methyl iodide to 120° – 130° for twenty-four hours and then distilled. The portion which passed over between 240° and 245° contained acetocinnamone, but only to the amount of 5 per cent. of the cinnamic aldehyde. Cinnamic aldehyde and methyl alcohol in equal numbers of molecules, boiled for a day with excess of zinc chloride, yielded a product containing acetocinnamone, but again only in very small quantity. The use of phosphoric anhydride also did not yield a favourable result.

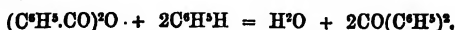
Phenyl-ethyl Ketone or Propiophenone, $C^9H^{10}O = C^6H^5.CO.C^2H^5$ (Th. D. Barry, *Ber.* vi. 1006; *Inaugural Dissertation*, Halle, 1874). This compound, prepared by distilling a mixture of calcium benzoate and propionate, boils at 210° and has a density of 1.01 at 22.5° . It does not unite with sodium bisulphite. Sodium-amalgam converts it into phenyl-ethyl carbinol, $C^9H^{12}.CHOH.C^2H^5$, boiling at 210° – 211° ; the pinacone of propiophenone is probably formed at the same time.

Nitropropiophenone, $C^9H^7(NO_2).CO.C^2H^5$, is formed in two modifications, crystalline and syrupy, according to the manner in which the nitration is effected. The crystallised modification is but slightly soluble in ether, alcohol, and benzene, nearly insoluble in water, melts at 100° and solidifies at 95° . By reduction it is converted into amidopropiophenone, which is syrupy in the free state, but yields a crystallisable hydrochloride, and a platino-chloride which forms granular crystals having the composition $[C^9H^7(NH_2).CO.C^2H^5.HCl]^2PtCl_4$.

Phenyl-propyl Ketone or Butyrophenone, $C^{10}H^{12}O = C^6H^5.CO.C^3H^7$ (Popoff, *Ber.* vi. 560; Schmidt a. Fieberg, *ibid.* 498). This ketone, prepared by distilling a mixture of calcium benzoate and butyrate, is an aromatic liquid having a density of 0.992 at 15° , and boiling at 218° – 221° (Popoff); density 0.990 at 15° ; b. p. 220° – 222° (S. and F.). It does not unite with sodium bisulphite; yields by oxidation benzoic and propionic acids (Popoff; S. and F.). When subjected to the regulated action of nitric acid, it yields nitro-derivatives; when the action is more violent, the product consists almost wholly of benzoic and nitrobenzoic acids. The ketone treated in alcoholic solution with sodium-amalgam is converted into the pinacone, $(C^6H^5.CH.C^3H^7)^2O$ —which is a solid body melting at 64° —and a liquid probably containing phenyl-pseudobutyl carbinol. With bromine a liquid bromo-compound is obtained which distils with vapour of water (Schmidt a. Fieberg).

Phenyl-isopropyl Ketone, $C^8H^8.CO.CH(CH^3)_2$, obtained in like manner with calcium isobutyrate and benzoate, boils at 209° – 217° , and yields by oxidation, benzoic, acetic, and carbonic acids (Popoff, *ibid.* 1255).

Diphenyl Ketone or Benzophenone, $C^{15}H^{12}O = C^6H^5.CO.C^6H^5$, is produced in abundance by heating a mixture of benzoic anhydride and benzene with phosphoric anhydride to 200° :



Pyrophosphoric acid may also be used as the dehydrating agent, but not boric anhydride, or dry hydrogen chloride (Kollarits a. Merz, *Ber.* vi. 446). The quantity obtained by heating benzene with benzoyl chloride in contact with zinc is but small (Grucarevic a. Merz, *ibid.* 60).

Diphenyl ketone heated with *hydriodic acid* and *amorphous phosphorus* is converted into diphenyl-methane, $CH_2(C^6H^5)_2$, and with zinc-dust into diphenyl-methane, tetraphenyl-ethane and tetraphenyl-ethylene (pp. 682, 683). By fusion with *potassium hydrosulphide* it is almost wholly converted into benzoic acid (Städel, *Ber.* vi. 178); by heating with *alcoholic potash* into diphenyl carbinol (Zagumenny, p. 682). Heated

with *fuming sulphuric acid*, it yields benzophenone-sulphonic acid, $\text{CO}(\text{C}^6\text{H}^4\text{SO}^3\text{H})_2$, and a body having the composition $\text{C}^{13}\text{H}^8\text{SO}^3$ (p. 682).

Chlordiphenyl Ketone or *Chlorobenzophenone*, $\text{C}^6\text{H}^4\text{Cl.CO.C}^6\text{H}^5$, is obtained, by heating chlorobenzene with benzoic anhydride and phosphoric anhydride, as an oily liquid which boils above 300° , solidifies quickly on cooling, and when recrystallised forms broad shining needles, which melt at 75.5 to 76° , dissolve with moderate facility in cold alcohol, sparingly in cold ligroin, easily in hot alcohol and ether (Grucarevic a. Merz).

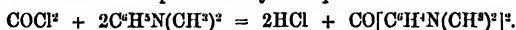
Bromodiphenyl Ketone, $\text{C}^6\text{H}^4\text{Br.CO.C}^6\text{H}^5$, obtained in like manner from bromobenzene, is crystalline, melts at 81.5° and distils without decomposition (Grucarevic a. Merz).

Attempts to prepare *cyanodiphenyl ketone* by similar means led only to the production of a polymeric cyanobenzene, agreeing in its properties with the so-called *cyaphenine* (iii. 449), which may also be obtained, without the aid of benzoic acid, by heating cyanobenzene to 200° with phosphoric anhydride.

Dinitrobenzophenone, $\text{C}^{13}\text{H}^8(\text{NO}^2)_2\text{O}$.—Benzophenone is not attacked by nitric acid of sp. gr. 1.4, and only imperfectly nitrated by fuming nitric acid at ordinary temperatures; but on heating it to 60° for $\frac{1}{2}$ to $1\frac{1}{2}$ hours with acid of sp. gr. 1.5 to 1.54, it is almost wholly converted into dinitro-compounds. By precipitating the product with water, washing, and crystallising it from glacial acetic acid, needles were first obtained melting at 189° – 190° ; afterwards (in larger quantity) laminæ, which when recrystallised from benzene or toluene yielded large plates melting at 148° – 149° . Both these products had the composition of dinitrobenzophenone. The toluene mother-liquor moreover deposited small prisms melting at 118° – 120° which were not analysed (? Doer's isodinitrobenzophenone, vii. 639). Both the above products (m. p. 189° – 190° and 148° – 149°) were likewise obtained when a substance melting at 127° – 129° , which was obtained by nitration of benzophenone and crystallisation from alcohol, was recrystallised from glacial acetic acid; they are also readily produced by nitration of diphenyl carbinol or benzhydrol (iv. 478). The needles melting at 189° – 190° were likewise obtained from diphenylmethane (Prætorius, Ber. x. 1855).

Diamidobenzophenone, $\text{C}^{13}\text{H}^8(\text{NH}^2)_2\text{O}$, is the compound, formerly called *Flavine*, which Chancel a. Laurent obtained by reducing dinitrobenzophenone with ammonium sulphide (ii. 656); it is more readily obtained by treating the dinitro-compound with tin and hydrochloric acid. It crystallises from hot water in slender yellow needles, melting at 165° . The *hydrochloride* forms small tablets; the *stannouschloride*, $\text{C}^{13}\text{H}^8(\text{NH}^2)_2\text{O}, 2\text{HCl}, 2\text{SnCl}^2$, crystallises in plates; the *acetyl-derivative* $\text{C}^{13}\text{H}^8(\text{NH.C}^2\text{H}^3\text{O})_2\text{O}$, in colourless needles melting at 226.5° (Stadel, Ber. xi. 744).

Tetramethyl-diamidobenzophenone, $\text{C}^{13}\text{H}^8[\text{N}(\text{CH}^3)_2]_2\text{O}$ or $\text{CO}[\text{C}^6\text{H}^4\text{N}(\text{CH}^3)_2]_2$, is the chief product of the action of carbonyl chloride on dimethylaniline in sealed tubes at about 120° ; its formation is represented by the equation:



The crude product is a dark grey crystal-pulp saturated with a blue colouring matter which produces a dark blue stain on wool and on the skin. The excess of dimethylaniline is removed by boiling with water, and the undissolved residue is washed on a filter and then treated with hydrochloric acid, which leaves a portion still undissolved. The hydrochloric acid solution gives with soda-ley a precipitate of tetramethyl-diamidobenzophenone. This compound possesses basic properties, dissolves readily in alcohol and ether, and crystallises from alcohol in yellow laminæ melting at 179° (uncor.) Its solution in hydrochloric acid gives with alcoholic platinum chloride small gold-yellow laminæ of the platinumchloride, $\text{CO}[\text{C}^6\text{H}^4\text{N}(\text{CH}^3)_2]_2, 2\text{HCl}, \text{PtCl}^4$ (W. Michler, Ber. ix. 716).

The portion of the crude product of the above reaction which is insoluble in hydrochloric acid, consists of hexmethyl-diamidobenzoyl-benzene, $\text{C}^6\text{H}^5\text{N}(\text{CH}^3)_2[\text{CO.C}^6\text{H}^4\text{N}(\text{CH}^3)_2]_2$, which is neither acid nor basic, and forms lemon-yellow monoclinic crystals melting at 122° (p. 1032).

The conditions under which one or the other of these bodies is more especially produced have been examined by Michler a. Dupertuis (Ber. ix. 1879). For the preparation of tetramethyldiamidobenzophenone, carbonyl chloride is passed into dimethylaniline at ordinary temperatures till the increase of weight equals the amount required by calculation; to obtain hexmethyltriamidobenzoylbenzene, on the other hand, the gas is passed into boiling dimethylaniline as long as it continues to be absorbed. When an alcoholic solution of tetramethyldiamidobenzophenone is boiled for a few hours with sodium-amalgam, the liquid evaporated to dryness, and the

residue washed with water and crystallised from ether, small colourless crystals are obtained melting at 96° , and possessing basic properties (probably the corresponding benzhydrol). They dissolve readily in ether and alcohol, and in the latter, as well as in glacial acetic acid, with a deep blue colour, which disappears on addition of an alkali.

When dimethylaniline and benzoyl chloride are heated together in a sealed tube to 150° – 180° , or boiled for several hours in a flask with reversed condenser, a thick crystalline mass is obtained; and on washing this mass with water, dissolving the oily layer in ether, drying it over calcium chloride; distilling—whereupon the greater portion passes over above 300° —and leaving it for a few days over sulphuric acid, the whole solidifies to a beautiful crystalline mass consisting of dimethyl-amido-dibenzoylbenzene, $\text{C}^6\text{H}^3\text{N}(\text{CH}_3)_2(\text{CO}.\text{C}^6\text{H}_5)_2$. This compound melts at 55° , and dissolves readily in alcohol and ether (Michler & Dupertuis).

Tetraphenyl-diamidobenzophenone, $\text{CO}[\text{C}^6\text{H}_4\text{N}(\text{C}^6\text{H}_5)_2]_2$, is obtained, together with hexathyl-triamidobenzoylbenzene (p. 1031), by saturating diethylaniline with carbonyl chloride, then adding half the original volume of diethylaniline, and heating the mixture in a sealed tube to 120° . The two bodies are separated in the same manner as the corresponding methyl-compounds.

Tetraphenyl-diamidobenzophenone forms small laminae melting at 95° – 96° . Its hydrochloride forms with platinic chloride a double salt, $\text{CO}[\text{C}^6\text{H}_4\text{N}(\text{C}^6\text{H}_5)_2]_2\text{HCl}.\text{PtCl}_4$, of a fine yellow colour (Michler & Gradman, *Ber.* ix. 1912).

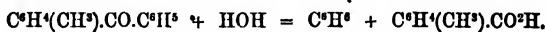
Action of Ammonia and Amines on Benzophenonic Chloride (Pauly, *Liebig's Annalen*, clxxvii. 198).—Benzophenone itself is not attacked by ammonia, or by aniline or its methylated derivatives, but these bodies act readily on the chloride $\text{C}^6\text{H}_5.\text{CCl}_2.\text{C}^6\text{H}_5$.

1. Alcoholic ammonia does not act on benzophenone even at 180° – 200° , but it acts energetically on the chloride (as formerly observed by Behr, *Ber.* iii. 791), producing benzophenone, sal-ammoniac, and perhaps also ethylamine hydrochloride, but not any ammonia-derivative of benzophenone. The chloride is not attacked by ammonia in ethereal solution, or (contrary to Behr's statement) by dry ammonia-gas.

2. *Action of Aniline*.—When 1 mol. benzophenonic chloride is added to 4 mols. aniline in a cooled vessel, the mixture solidifies to a crystalline mass; and on treating this mass with water and ether, aniline hydrochloride dissolves in the water, while the ether takes up diphenylmethyleno-aniline, $\text{C}^{12}\text{H}_9\text{N}=(\text{C}^6\text{H}_5)_2\text{C}=\text{NC}^6\text{H}_5$ (see PHENYLAMINES).

Dimethylaniline acts on benzophenonic chloride only with the aid of heat, yielding as final product a dark-red syrupy liquid which yields to ether a base having the composition $\text{C}^{21}\text{H}^{18}\text{N}$. Diphenyl-methyleno-toluidine, $(\text{C}^6\text{H}_5)_2\text{C}=\text{N}.\text{C}^6\text{H}_4$, and diphenyl-methyleno-naphthylamine, $(\text{C}^6\text{H}_5)_2\text{C}=\text{N}.\text{C}^{10}\text{H}_7$, are produced similarly to diphenyl-methyleno-aniline, by treating benzophenonic chloride with paratoluidine and naphthylamine respectively. See PHENYLAMINES.

Tolyl-phenyl Ketones, $\text{C}^6\text{H}_4(\text{CH}_3).\text{CO}.\text{C}^6\text{H}_5$. Two of these compounds are known, one solid and the other liquid. The solid modification is *paratolyl-phenyl ketone*, having the methyl of the group $\text{C}^6\text{H}_4(\text{CH}_3)$ in the para-position with respect to the CO-group, inasmuch as it is resolved by heating with soda-lime into benzoic acid and para-toluic acid:



The liquid ketone appears to be a mixture of the *o*- and *m*- modifications (see BENZOYL-BENZOIC ACID, p. 309).

Zincke, by oxidising benzyl-toluene, $\text{C}^6\text{H}_4(\text{CH}_3).\text{CH}_2(\text{C}^6\text{H}_5)$, with chromic acid, obtained a mixture of tolyl-phenyl ketone and benzoyl-benzoic acid (resulting from further oxidation); and on dissolving out this acid with caustic soda, and purifying the residue by solution in hydrochloric acid, agitation with ether, fractional distillation, &c., tolyl-phenyl ketone was obtained in the form of an oily liquid, which became viscous at low temperatures, but did not solidify (vii. 177).

Kollarits & Merz (*Ber.* vi. 446), by heating benzoic acid with toluene and phosphoric anhydride (p. 149), obtained the ketone in the form of a liquid which solidified after standing for some months, or more quickly on the introduction of a crystal. According to Thörner (*Liebig's Annalen*, clxxxix. 83) the best proportions for the preparation of the solid ketone are 3 parts benzoic acid, 4 toluene, 4 phosphorus pentoxide, and 4 sand, the mixture being heated in sealed tubes for eight or ten hours to 200° – 220° . On subjecting the product to fractional distillation, the fraction 300° – 305° solidified immediately in the crystalline form, and was easily obtained pure by recrystallisation from ether-alcohol. By this process 1000

grams of benzoic acid yielded 330 of pure paratolyl-phenyl ketone and 402 of the liquid compound still containing some of the solid.

Paratolyl-phenyl ketone crystallises in thick colourless prisms, melts at 56.5° – 57° , dissolves sparingly in cold ligroin, with moderate facility in cold alcohol, easily in ether and in benzene. After fusion it often remains fluid for a long time and easily forms supersaturated solutions (Kollarits & Merz).

Chlorinated Derivatives.—Paratolyl-phenyl ketone heated with phosphorus pentachloride appears to be converted into the corresponding ketonic chloride, $C^6H^3.CCl^2.C^6H^5$; but this compound decomposes on distillation and has therefore not been isolated. When the ketone is heated in dry chlorine gas, the hydrogen in the methyl-group is more or less replaced by chlorine, and by regulating the temperature and the proportion of chlorine, the three following chlorides may be obtained.

Parabenzoyl-benzyl Chloride, $C^6H^5.CO.C^6H^4.ClH^2Cl$, is formed at 100° – 110° , and purified by crystallisation from alcohol and washing with ether, which removes some dichloride. It forms long white prisms melting at 97° – 98° . On adding a little water to its solution in absolute alcohol it crystallises in long, slender, silky needles. It is readily soluble in chloroform, carbon sulphide, benzene, toluene, hot alcohol, and glacial acetic acid, more sparingly in cold alcohol and ether. It can be sublimed, and easily undergoes double decomposition.

Parabenzoylbenzylene dichloride, $C^6H^5.CO.C^6H^4.ClHCl^2$, is produced by the continued action of chlorine at 130° – 140° , and crystallises from alcohol and acetic acid in silky plates, melting at 94° – 95° . It dissolves easily in the same solvents as the monochloride, and also in ether. It can be sublimed, and boiling alkalis convert it slowly into parabenzoylbenzoic acid. When it is heated with alcohol and silver nitrate, or with water and silver oxide or lead oxide, the same acid is formed, and not the aldehyde.

Parabenzoylbenzenyl trichloride, $C^6H^5.CO.C^6H^4.CCl^3$, is formed at 150° – 160° ; like the preceding compound it is best purified by the fractional precipitation of its boiling solution in glacial acetic acid with water. It crystallises in small glistening plates or larger thin square plates, melting at 111° – 111.5° . It does not dissolve very freely in cold alcohol and acetic acid, but readily in the hot liquids and in the solvents mentioned above. It can be sublimed, and on heating it with water or silver nitrate to 170° – 180° , or boiling it with alkalis, it is converted into parabenzoylbenzoic acid. On heating it with phosphorus pentachloride, it is converted into $C^6H^5.CCl^2.C^6H^4.CCl^3$, which is readily soluble in acetic acid, carbon sulphide, benzene, &c. It crystallises in square striated thin plates, melting at 78° – 80° ; it cannot be sublimed, and is converted into parabenzoylbenzoic acid by concentrated nitric acid, and by boiling it with alkalis.

Paratolyl-phenyl Pinacolins, $C^{12}H^{24}O$.—Two of these bodies, α and β , are formed by the action of zinc and hydrochloric acid on the ketone.

The α -pinacolin, which is the first product, is easily converted into the β -compound, and therefore obtained pure only by working under certain conditions. A good yield is obtained by dissolving 10 grams of the ketone in 500 c.c. of alcohol of 75 per cent., and adding it to a mixture of zinc and so much hydrochloric acid that a brisk evolution of hydrogen goes on in the cold. The liquid is then boiled for two or three hours, and the pinacolin which has separated out is purified by crystallising it from alcohol. It forms microscopic glistening needles, melting at 214° – 215° , and dissolves freely in chloroform, carbon sulphide, toluene, and boiling acetic acid, less readily in boiling alcohol and ether, very sparingly in cold alcohol.

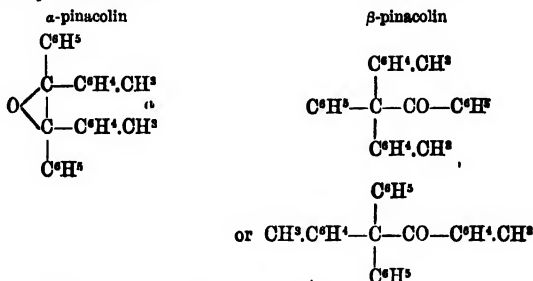
The β -pinacolin is much more easily obtained by using a stronger alcoholic solution of the ketone, and allowing the reaction to go on for four or five days. It crystallises from hot absolute alcohol in strongly refractive, small square plates, which become opaque on drying, and turn yellow on exposure to light. It dissolves readily in the same liquids as the α -compound, also in boiling alcohol. When the α -pinacolin is heated with benzoyl chloride or with concentrated hydrochloric acid to 150° – 160° , or with glacial acetic acid to 170° – 180° , it is converted into the β -compound. The α -compound is scarcely acted upon by boiling with nitric acid, an aqueous solution of chromic acid, or potassium permanganate, but a boiling solution of chromic trioxide in acetic acid oxidises it again to paratolylphenyl ketone.

The β -pinacolin cannot be converted into the α -compound; on heating it or the latter with concentrated hydriodic acid and amorphous phosphorus to 210° – 220° , the hydrocarbon, $C^{22}H^{22}$, is formed, which is readily soluble in chloroform, carbon sulphide, and toluene, but very sparingly in cold alcohol and ether. It separates from boiling alcohol or acetic acid in microscopic, probably triclinic crystals, melting at 213° – 213.5° .

On boiling the β -pinacolin with glacial acetic acid and chromic trioxide, a large

portion is completely burnt to carbon dioxide, and only a small quantity of an acid is obtained having the formula $C^{11}H^{18}O^2$, or more probably $C^{22}H^{36}O^2$, some benzoic acid being formed at the same time. This acid separates from ether as an amorphous transparent mass, and is precipitated from an ammoniacal solution by hydrochloric acid, as a bulky, amorphous white powder. It dissolves freely in ether, benzene, alcohol, glacial acetic acid, &c., melts at 78° – 83° , and cannot be sublimed. Its alkaline solution is precipitated by carbon dioxide; the salts which it forms with the alkali-metals are amorphous and deliquescent; the other salts are gelatinous precipitates.

From these results it appears most probable that, by the action of nascent hydrogen on the ketone, first the corresponding pinacone is produced, which, however, at once loses the elements of water and is converted into the α -pinacolin. As this compound can be easily reconverted into the ketone, it must have a similar constitution, while the β -compound, which by oxidation loses carbon and yields a monobasic acid, is produced by an intramolecular change, and its constitution is therefore probably similar to that of ordinary pinacolin from acetone, which by oxidation yields trimethyl-acetic acid.



Cymyl-phenyl Ketone, $C^{10}H^{13}.CO.C^6H^5$, is formed in small quantity by heating a mixture of cymene and benzoic acid, or benzoyl chloride, with phosphoric anhydride. It is a slightly yellow, very fragrant oil, which boils at 140° , and does not solidify in a freezing mixture (Kollarits a. Merz, *Deut. Chem. Ges. Ber.* vi. 546; Grucarevic a. Merz, *ibid.* 1244).

Dibenzyl Ketone, $(C^6H^5)CH^2.CO.CH^2(C^6H^5)$. This compound, heated to about 180° with hydriodic acid and amorphous phosphorus, yields a viscid product, solidifying on addition of soda to a crystalline pulp, from which ether extracts dibenzyl-methane, $C^{13}H^{16} = CH^2(CH^2.C^6H^5)^2$, forming about a third of the entire product (p. 640). The remainder consists of a phosphorised acid, $C^{13}H^{17}PO^3 = C^{13}H^{15}.PO.(OH)^2$, related to dibenzyl-methane in the same manner as phosphenylic acid, $C^6H^5.PO.(OH)^2$, to benzene (Graebe, *Ber.* vii. 1623). See p. 640.

Naphthyl Ketones (Kollarits a. Merz, *Ber.* vi. 541; Grucarevic a. Merz, *ibid.* 966, 1238).

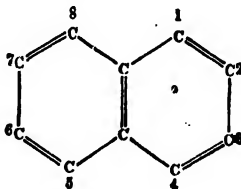
Naphthyl-phenyl Ketone, $C^{10}H^7.CO.C^6H^5$.—Two isomeric forms of this compound, α and β , are produced by heating a mixture of naphthalene and benzoic acid with phosphoric anhydride, to 200° – 220° for ten or twelve hours. The viscid product is exhausted with benzene, and the solution submitted to fractional distillation, whereupon it yields above 300° , a thick reddish-yellow oil, which when rectified yields a mixture of the two naphthyl-phenyl ketones. This liquid first deposited slender needles, which, when purified by washing with alcohol and crystallisation from ether-alcohol, melted at 82° ; afterwards mixtures from which, by solution in ether-alcohol, short prisms and needles were obtained, and these were further separated by sifting through a fine sieve which allowed only the needles to pass. The short prisms which melted at 75.5° were likewise obtained by heating a mixture of α -naphthoic acid and benzene with phosphoric anhydride, and may, therefore, be designated as α -naphthyl-phenyl ketone. The needles, melting at 82° , and identical with those above mentioned, were obtained in like manner from β -naphthoic acid and benzene, and may, therefore, be called β -naphthyl-phenyl ketone: from the resulting oil they are most easily separated by solution in ether, addition of alcohol, and re-crystallisation of the powder which separates as the ether evaporates. The β -modification is somewhat less soluble than the α in cold alcohol (α in 41, β in 49 pts.); they are both more readily soluble in hot alcohol, also in ether and in benzene; both are nearly inodorous, and volatilise without decomposition.

Dinaphthyl Ketones, $C^{10}H^7.CO.C^{10}H^7$.—Two of these ketones are known, and may be distinguished by the letters a and b . The a -modification is obtained by

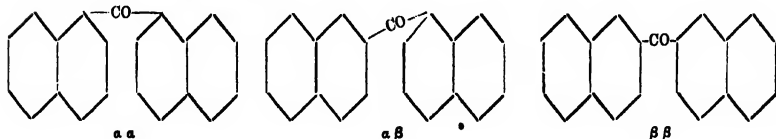
heating a mixture of α -naphthoic acid and naphthalene with phosphoric anhydride, as an oil which solidifies after a while to a vitreous mass. By dissolving this product in ether, adding alcohol, and recrystallising the precipitate from ether-alcohol, it is obtained in crystals melting at 130° . It dissolves at 14° in 77 parts of absolute alcohol; more easily in hot alcohol, ether, and benzene; crystallises from boiling alcohol in colourless pointed needles; from ether-alcohol in thick prisms and tablets (Kollarits a. Merz). Grucarevic a. Merz (*Ber.* vi. 1238) prepare the same compound by boiling α -naphthoyl chloride with excess of naphthalene, and introducing into the liquid a thin strip of zinc; an excess of zinc must be avoided. The product yields by distillation a brown oil which soon solidifies; and by dissolving the mass in warm chloroform and adding ether-alcohol, prisms of the α -ketone are first obtained, melting at 135° ; afterwards mixtures of this compound with another which crystallises in reddish scales. The quantity of α -naphthyl ketone obtained by this process amounts to between $\frac{1}{2}$ and $\frac{1}{3}$ of the naphthoyl chloride used, and is larger than that produced from an equal weight of naphthoic acid.

b-Dinaphthyl Ketone.—Kollarits a. Merz prepared this modification from β -naphthoic acid and naphthalene, and after repeated crystallisation from various solvents, obtained it in needles which sintered together at 123° , melted at 135° , and were altogether less soluble than the α -ketone. Grucarevic a. Merz prepared it from naphthalene and β -naphthoyl chloride in quantity amounting to about $\frac{5}{6}$ of the latter; and by repeatedly crystallising the crude product from chloroform and ether, white shining laminae were obtained melting at 164.5° , together with white needles having the same composition but melting at 125.6° . The former dissolved at 19° in 1256 parts, the latter in 267 parts of alcohol.

Naphthalene, as already explained (vi. 212), may be represented by the following constitutional formula:



in which the positions 1, 4, 5, 8 are similar to one another, but different from the positions 2, 3, 6, 7, which are also similar among themselves. Naphthalene mono-derivatives (chloro-, nitro-naphthalenes, &c.) in which the substituted radicle occupies one of the positions 1, 4, 5, 8, are called α -derivatives; those in which it occupies either of the other four positions are called β -derivatives. This being understood, it is easy to see that dinaphthyl ketone, $\text{C}^{10}\text{H}^7\cdot\text{CO}\cdot\text{C}^{10}\text{H}^7$, is susceptible of three modifications, $\alpha\alpha$, $\alpha\beta$, $\beta\beta$; thus:



Now, according to Grucarevic a. Merz (*Ber.* vi. 1246), α -dinaphthyl ketone, finely triturated with soda-lime and heated for eight hours in a sealed tube to about 350° , is resolved into naphthalene and a mixture of α - and β -naphthoic acids: hence it must be the $\alpha\beta$ -modification. β -dinaphthyl ketone (both modifications, m. p. 125.6° and 164.5°) is resolved by heating with soda-lime into naphthalene and β -naphthoic acid; and since this latter can be formed only from a dinaphthyl ketone having the CO-group attached to one of its β -positions, and moreover the $\alpha\beta$ -modification has been shown to be that which is designated as α -dinaphthyl ketone, it follows that both the β -modifications must have the $\beta\beta$ structure, and can therefore be only physical isomerides.

In α -naphthyl-phenyl ketone, the CO-group is attached on the one side to either of the α -carbon-atoms of the naphthalene-molecule, and on the other to either of the carbon-atoms of the benzene-molecule; similarly with regard to β -naphthyl-phenyl ketone.

KINOIN, $\text{C}^{14}\text{H}^{12}\text{O}^6$ (Etti, *Berl. Ber.* xi. 1879). When Malabar Kino is boiled with twice its weight of dilute hydrochloric acid (1 : 6), and the solution decanted

from the deposit of kino-red is shaken up with ether, a solution is obtained which, on evaporation, leaves kinoïn in the form of a reddish crystalline substance; and by repeatedly crystallising this substance from a small quantity of water, pure colourless crystals of kinoïn are obtained, to the amount of about 15 grams from a kilogram of kino.

Kinoïn is anhydrous; it dissolves sparingly in cold water, easily in hot water and in alcohol. The solutions may be evaporated without alteration, but decompose on exposure to the air. Kinoïn heated to 120° – 130° till its weight becomes constant yields the anhydride, $C^{28}H^{22}O^{11} = 2C^{14}H^{12}O^6 - H^2O$, which appears to be identical with kino-red; and this anhydride heated to 160° – 170° loses another molecule of water and is converted into $C^{28}H^{20}O^{10}$. Both these anhydrides are precipitated by gelatin; kinoïn itself is not.

When kinoïn is heated to 120° – 130° in a sealed tube with strong hydrochloric acid, methyl chloride escapes on opening the tube, and a solution is formed containing pyrocatechin and gallic acid: hence it may be inferred that kinoïn has the constitution of *methyl-pyrocatechyl gallate*, $C^7H^4(CH^3)(C^6H^3O)O^5$.

Kino-red yields by dry distillation a small quantity of watery and oily distillate, the greater part of the substance however becoming carbonised. The oily distillate yields by fractional distillation pyrocatechin and phenol, mixed with small quantities of an ethereal compound, probably anisole or guaiacol.

KJERULFIN. A mineral from Banile in Norway, occurring massive, with imperfect cleavage in two directions at right angles to one another. Fracture uneven and splintery. Lustre, fatty. Colour, pale red. Translucent in thin fragments. Sp. gr. = 3.15. Hardness = 4.5. Exhibits faint white phosphorescence when heated. Fusibility about 3; melts with some intumescence to a blistered enamel. Easily soluble in hot concentrated hydrochloric acid; somewhat less easily in nitric acid. With sulphuric acid it evolves hydrofluoric acid, while calcium sulphate separates. Analysis gave:

P ² O ⁵	MgO	CaO	Na ² O	Fl	SiO ²	Al ² O ³
42.22	37.00	7.56	1.56	4.78	1.50	5.40 = 100.02

with traces of potassium, iron, and sulphuric acid.

When the non-essential constituents are deducted, this composition corresponds with the formula $2Mg^3(PO^4)^2 + CaF^2$, a small portion of the calcium being replaced by sodium.

Kjerulfin differs from wagnerite, which it resembles in many respects, by containing less fluorine and sodium, and more calcium, so that its solution in hydrochloric acid gives a precipitate with sulphuric acid, which is not the case with wagnerite.

KLINO HUMITE or **CLINO HUMITE.** See HUMITE (p. 1044).

KÖNIGINN. A mineral from Russia belonging to the Brochantite group (p. 349).

KOPPITE. This name is given by A. Knop (*Jahrb. f. Min.* 1875, 67) to a variety of pyrochlore from the limestones of the Kaiserstuhl, which he regards as a distinct mineral species, on account of the smallness of its amount of fluorine (1.28 to 1.82 per cent.), and the absence of titanate acid and thorina.

KOSIN, $C^{31}H^{22}O^{10}$ (Flückiger a. Buri, *Arch. Pharm.* [3], v. 193; *Pharm. J. Trans.* [3], v. 562). A substance obtained from the flowers of the koso tree of Abyssinia (*Hapiria abyssinica Lamarek*), and supposed to be the principle to which the anthelmintic properties of these flowers are due. It has a sulphur-yellow colour; crystallises in rhombic forms; dissolves at 15° in strong sulphuric acid, and crystallises unaltered on cooling; melts but does not give off water at 142° ; and at higher temperatures emits an odour of butyric acid and yields a brown tar. It is nearly insoluble in water, but easily soluble in ether, benzene, carbon sulphide, chloroform, glacial acetic acid and alcohol; dissolves also in aqueous alkalis and alkaline carbonates, and is precipitated therefrom by acids. Ferric chloride added to the alcoholic solution produces, after a while, a permanent red coloration.

Kosin dissolves in strong sulphuric acid, forming isobutyric acid and a red amorphous body, which has the composition $C^{22}H^{21}O^{10}$ [$2C^{22}H^{20}O^{10}$], or $C^{22}H^{22}O^{10}$, accordingly as it is prepared with cold or with warm sulphuric acid.

Kosin fused with potash produces formic, butyric and oxalic acids, together with a brown unctuous substance. With *sodium-amalgam* it yields a volatile oil, $C^{23}H^{16}O^2$, and an amorphous substance having the colour of stannic sulphide, and the empirical formula $C^4H^4O^2$. *Acetic anhydride* converts kosin into acetyl-kosin, $C^{31}H^{22}(C^2H^3O)^4O^{10}$. From these results Flückiger a. Buri regard kosin as an ether of isobutyric acid.

The substance called *Koussin* or *Tienin*, which Pavet and Bedall obtained from

the flowers of *Brayera anthelmintica* (v. 654), is, according to Flückiger a. Buri, a mixture containing variable quantities of pure kosin.

KOUMISS. Observations on the preparation of this beverage have been published by J. T. George (*Pharm. J. Trans.* [3], iii. 544; *Jahresh. f. Chem.* 1873, 1080), and a continuation of former observations (vii. 715), by Jagielski (*American Chemist*, v. 448).

• **KRYOKONITE.** See CRYOCONITE (p. 589).

KUNKUR. An argillaceous sedimentary limestone occurring in India, and used for the preparation of mortar. Recently burnt kunkur-stone was found to contain 40.0 per cent. silicates, 8.8 calcium carbonate, and 51.2 quicklime. This lime possesses considerable hydraulic properties. When slaked it increases greatly in bulk, its density diminishing from 1 to 0.67. To form the mortar, slaked kunkur lime is mixed with sand in such proportion as to form a mixture having the following composition reckoned on the dry mass:

1 vol. lime, weighing 0.67	{ 0.33 Silicates
2 vols. sand „ 3.00	{ 0.34 Lime
	<hr/>
	3.67

This mortar therefore contains scarcely 10 per cent. of its dry weight of lime. Nevertheless it hardens under water to such a degree, that after a month it is able to bear a weight of 15 pounds on the square inch (E. Nicholson, *Chem. News*, xxxii. 82).

L

LABRADORITE. See FELSPAR (p. 774).

LAC. Japanese lac is described by Wagner (*Dingl. pol. J.* ccxviii. 361, 452). It is obtained from the juice of a species of Sumach (*Rhus vernicifera*), growing chiefly in the district of Yoshino, by making incisions in the bark. The viscid juice, which, on exposure to the air, quickly becomes dark-coloured and covered with a crust, is known by the name of *Urushi*. The value of the lac varies according to the season in which it is collected, the best being obtained towards the end of August. A well-grown tree yields about 375 grams of juice, and then dies. The juice is filtered through a peculiar kind of paper made in Yoshino. It is only the red lac (coloured by cinnabar) that retains its colour; all other shades become deteriorated by the darkening of the lac on exposure to the air. Black lac is produced by stirring the juice for a day in contact with the air, after adding to it a certain quantity of water which has stood over iron filings. Lacs which are to be polished after hardening have only a small quantity of oil added to them; others are mixed with one-fifth of an oil obtained from the Ye plant (*Perilla ocimoides*). The working of this lac is a somewhat unhealthy occupation, the vapours emitted from the juice producing painful cutaneous eruptions.

In articles to be coated with this lac, all cracks and holes must be stopped with linen or cotton soaked in a quickly hardening lac (Seschine lac from the twigs of *Rhus vernicifera*). A thin cloth or a layer of the long-fibred Yoshino paper is then immediately attached to the surface with Seschine lac; on this is laid a coating of the same lac mixed with powder of burnt clay; and the articles are left for twenty-four to forty-eight hours in a dark moist place for the lac to harden. The hardened coating is next rubbed with a soft stone, after which a second layer of fine tripoli and lac is laid on, and this, when hardened, is rubbed with charcoal and water. The surface thus prepared is ready to receive the true lac. At first a few layers of a cheaper lac are laid on and finally the best coloured lac, each layer, after hardening, being rubbed with a smooth piece of charcoal and water. Lastly, to produce the lustre, a very thin coating of Seschine lac is laid on the object by means of a cotton pad, and polished, when dry, with very fine powder of stag's horn or burnt bones, rubbed on with the finger or the palm of the hand.

On Japanese lac, see further Robertson (*Pharm. J. Trans.* [3], vi. 487). On Chinese lac, see *American Chemist*, v. 453.

LACTIC ACID, $C^3H^4O^3$. The isomeric modifications of this acid have been further examined by Wislicenus (*Liebig's Annalen*, clxvi. 3; clxvii. 302, 346).

1. **Hydracrylic Acid**, produced by the action of silver oxide on β -iodopropionic acid, $CH^2I.CH^2.COOH$, is not identical with ethylene-lactic acid, as might be supposed from its mode of formation, but a modification distinct from both ethylene-lactic and ethylidene-lactic acids, and represented by the formula $CH^2OH.C \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} CHO$ (*ibid.* 718).

2. **Sarcolactic Acid.** The more recent experiments of Wislicenus confirm the view formerly suggested (*loc. cit.*) that sarcolactic acid is a mixture of two distinct acids, the more abundant of which, called paralactic acid, turns the plane of polarisation to the right and forms well-crystallised salts, whereas the other, which is present in much smaller quantity, and is probably the true ethylene-lactic acid, exhibits but very little crystallising power.

To separate the two acids, sarcolactic acid, prepared from extract of meat, was saturated with zinc carbonate, and the concentrated solution was precipitated with four or five times its volume of alcohol of 90 per cent. The paralactate was thereby precipitated as a bulky mass of very small colourless crystals, which afterwards became denser; these were washed with alcohol and pressed, then several times dissolved in water and precipitated by alcohol, and finally recrystallised from boiling water. The quantity of pure zinc salt thus obtained amounted on the average to 2 per cent. of the meat-extract used. The alcoholic mother-liquors contained chiefly the zinc salt of the second constituent of sarcolactic acid. Of the properties formerly attributed to zinc paralactate (iii. 459, 460), chiefly according to the experiments of Engelhardt (*Liebig's Annalen*, lxx. 359), two only have been confirmed by Wislicenus, viz. the amount of crystallisation-water, which agrees with the formula $C^3H^{10}ZnO^6.2H^2O$, and the tendency of the salt to form distinct crystals, whereas the fermentation lactate tends rather to form groups or crusts of crystals. On the other hand, all the earlier determinations of solubility of this salt appear to have been made with supersaturated solutions; and Wislicenus finds that the amount of water in a solution prepared with the aid of heat, and left to cool in contact with the crystals which separate, decreases continually, and does not attain a constant value till after about a month, this value agreeing with a solubility of 1 pt. of the crystallised salt in about 17.5 pts. water at 14° – 15° (1 pt. fermentation lactate requires for solution 58 to 63 pts. water). In boiling alcohol, zinc paralactate dissolves in the proportion of about 1 : 1000, and in much smaller proportion in cold alcohol. *Calcium paralactate* has the composition $2C^3H^{10}CaO^6.9H^2O$.

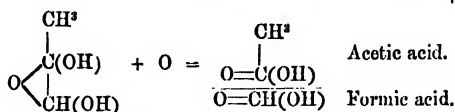
The conversion of sarcolactic acid into the anhydride of fermentation lactic acid [dilactic acid, $C^3H^{10}O^3 = 2C^3H^4O^3 - H^2O$] was observed by Strecker in 1858 (iii. 457). Wislicenus finds that when pure paralactic acid is heated for some time in a retort at 135° , a small quantity of it distils unaltered, together with the water, and the residue contains dilactic acid, the quantity of which increases as the heating is continued, so that after a few days the residue consists almost exclusively of it. The same acid, heated to 150° in a current of air, was, for the most part, converted into ordinary lactide, $C^3H^4O^3$, melting at 124.5° . Optically active lactic acid, therefore, when heated to 135° – 150° , is gradually but completely converted into the anhydrides of optically inactive fermentation-lactic acid. Paralactic acid left in a perfectly dry atmosphere at ordinary temperatures, is dehydrated exactly in the same manner as ordinary lactic acid, that is to say, it is converted first into dilactic acid and then into lactide (vii. 720). The mixture of the anhydrides of dextrogyrate paralactic acid possesses a high degree of levogyrate power. A preparation which had been kept over sulphuric acid for 21 months, and then consisted of 84.19 per cent. dilactic acid and 16.04 lactide, exhibited in alcoholic solution, for the line D, a specific rotatory power of -85.80° to -85.93° . This residue, boiled for a long time with zinc carbonate, was converted into a mixture of salts, in which the paralactate greatly predominated.

The optical rotatory power of paralactic acid, in a specimen which had been prepared by dehydration at ordinary temperatures, and contained 0.0738 gram of acid in a cubic centimeter, was found to be $[\alpha]_D = 2.78$. It did not, however, remain constant, but decreased suddenly and considerably after every further addition of water, and the more considerably in proportion as the original solution was more concentrated; after some time it gradually increased again, without, however, regaining its original value. The rotatory power of the metallic paralactates is of opposite sign to that of the free acid; that of the zinc salt being smaller in supersaturated than in normal solutions, in which latter $[\alpha]_D = -7.6^{\circ}$ to -7.7° for the crystallised salt. For the crystallised calcium salt, $[\alpha]_D = -3.87^{\circ}$.

Paralactic acid heated alone to 140° – 150° is resolved, like the fermentation acid,

into formic acid and acetaldehyde. By oxidation with a slight excess of potassium dichromate and sulphuric acid (1 at. disposable oxygen to 1 mol. lactic acid) it yields acetaldehyde, together with formic, acetic, and carbonic acid, but neither malonic nor oxalic acids.

The production of formic and acetic acids by the oxidation of paralactic acid is easily explained if the latter be represented by the formula, $\text{CH}^3-\text{C}(\text{OH})-\text{CH}(\text{OH})$, thus:

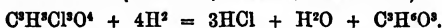


On this view, paralactic acid would be related to ethylidene-lactic acid in the same manner as hydracrylic to ethylene-lactic acid. As, however, hydracrylic acid—the formula of which is better established than that of paralactic acid—does not exhibit circular polarisation, Wislicenus thinks it preferable to assign to paralactic acid the same constitutional formula as to ethylidene-lactic acid, regarding these two acids as physical isomerides (vii. 720).

Ethylene-lactic Acid, $\text{CH}^3\text{OH}.\text{CH}^2.\text{COOH}$. This acid, whether prepared from sarcosolactic acid, or synthetically by combining ethylene with carbonyl chloride, and decomposing the resulting chloride, $\text{CH}^3\text{Cl}.\text{CH}^2.\text{COCl}$, with an alkali, or by either of the other processes already given (vi. 770), is very difficult to purify, being mixed in the first case with paralactic acid, and in the case of the synthetical preparation, with ethylidene-lactic acid, formed at the same time by intramolecular transposition. It may, however, be obtained quite pure by digesting its zinc salt—previously freed as far as possible from ethylidene-lactate or paralactate respectively by the difference of solubility of these salts in water (vii. 719)—with quantities of nearly absolute alcohol not sufficient to dissolve the whole of it, or by fractionally precipitating its alcoholic solution with ether. The zinc salt, either of the synthetically formed acid or of that prepared from different animal fluids, is thus obtained in the form of a brittle transparent gum which deliquesces in contact with the air.

Pure ethylene-lactic acid is not converted by hydriodic acid into β -iodopropionic acid, and does not yield a sparingly soluble zinc-calcium salt. By oxidation with chromic acid, it yields large quantities of carbon dioxide and oxalic acid, and a small quantity of malonic acid, but no formic acid (Wislicenus, *Annalen*, clxvii. 346; *Ber.* vi. 1395).

Ethylidene-lactic acid is produced by prolonged boiling of isotrichloroglyceric acid with tin and hydrochloric acid (Schroeder, *Annalen*, clxxvii. 282):



Iodo-lactic acid, $\text{C}^3\text{H}^3\text{IO}^3$, is prepared by heating chlorolactic acid to 50° with potassium iodide. It melts at 84° – 85° , and forms a zinc-salt crystallising in tablets (Glinsky, *Berl. Ber.* vi. 1257).

LACTIC ETHERS, CHLOR- and BROMINATED (L. Henry, *Ber.* vii. 762). Ethyl lactate unites with chloral gradually and with slight elevation of temperature, forming a viscid liquid which, when treated with phosphorus pentachloride, yields ethylic tetrachlorethyl-lactate, $\text{CH}^3-\text{CHO}(\text{CHCl}.\text{CCl}^3)-\text{COOC}^2\text{H}^5$, a thick, colourless, non-distillable liquid, having a peculiar odour, sweetish taste, and sp. gr. = 1.42 at 11° .

Trichlorethylidenic Lactate, $\text{C}^3\text{H}^3\text{Cl}^3\text{O}^3 = \text{CH}^3.\text{CH} \begin{array}{c} \text{CO.O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH}.\text{CCl}^3$, is formed by heating lactic acid with chloral in a sealed tube to 150° – 150° , and passes over on distilling the product with steam, as an oil which has a peculiar odour, is nearly insoluble in water, and, after drying with calcium chloride, solidifies in splendid crystals. It melts at 45° , boils without decomposition at 222° – 224° , dissolves easily in alcohol, ether, and carbon sulphide (Wallach a. Heymer, *Ber.* ix. 545).

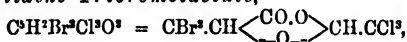
Trichlorethylidenic Trichlorolactate, $\text{CCl}^3.\text{CH} \begin{array}{c} \text{CO.O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH}.\text{CCl}^3$, or *Chloralide*, is formed in like manner by heating chloral with trichlorolactic acid (p. 445 of this volume).

Chloralide crystallises in splendid monoclinic crystals, often more than an inch long. Axes $a : b : c = 1.2038 : 1 : 0.3620$. Angle $ac = 84^\circ 52'$. Observed forms, $\infty P \infty$, $\infty R \infty$, ∞P , ∞P^2 , $0P$, $R \infty$. Angle $\infty P : \infty P = 100^\circ 33'$; $R \infty : R \infty = 89^\circ 40'$; $R \infty : \infty P \infty = 85^\circ 10'$. Cleavage perfect, parallel to $\infty R \infty$. Plane of optic axes perpendicular to the clinopinacoid. The median line situated in the plane of symmetry forms with the vertical in the acute angle of the axes a and c , for Li-red

11° 34', for Na-yellow 11° 44'. The median line parallel to the axis *b* exhibits negative double refraction and crossed dispersion; the axial angle in oil is for Li 99° 27', for Na 99° 51' (Bodewig, *Zeitschr. f. Krystallographie*, i. 594).

Tribromomethylidene Tribromolactate, or *Bromalide*, $C^3H^2Br^2O^3 = CBr^3 \cdot CH \begin{smallmatrix} CO.O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CH.CBr^3$, is obtained in like manner from tribromolactic acid and bromal, and by heating bromal with fuming sulphuric acid (Reincke, *Berl. Ber.* 1216). It melts at 158° (Wallach a. Reincke, *ibid.* x. 2128).

Trichlorethylidene Tribromolactate,

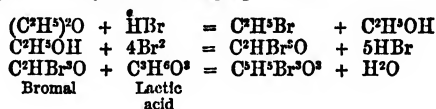


from tribromolactic acid and chloral, melts at 132°–135°. *Tripromethylidene*

Trichlorolactate, $CCl^3 \cdot CH \begin{smallmatrix} CO.O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CH.CBr^3$, from trichlorolactic acid and bromal, melts at 149°–150°. *Tribromomethylidene Lactate*, $C^3H^2Br^2O^3 =$

$CH^3 \cdot CH \begin{smallmatrix} CO.O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CH.CBr^3$, from lactic acid and bromal, melts at 95°–97° (Wallach a. Reincke). This last compound, called by Klimenko *lactide bromal*, is also formed by dropping bromine into a solution of lactic acid in twice its volume of ether. A brisk action then takes place, which must be moderated by cooling; and after 2 mols. bromine have been added, the liquid is heated on the water-bath in a vessel with reversed condenser, till that which runs back exhibits a yellowish colour. A large quantity of hydrogen bromide is then given off, and considerable quantities of ethyl bromide pass over in the subsequent distillation. Crystals form in the residue on standing, and on adding water, a thick oil separates, which after a while solidifies to a crystalline mass. The crystals, which have a strong pungent odour, may be purified by washing with water, pressing, and recrystallisation from hot alcohol. They have then a neutral reaction, an agreeable though pungent odour, and agree in composition with the formula of tribromomethylidene lactate, $C^3H^2Br^2O^3$.

The formation of this compound by the action of bromine on lactic acid in presence of ether, may be represented by the following equations:



Tribromomethylidene lactate is insoluble in water, very slightly soluble in cold, much more readily in hot alcohol, and separates therefrom on cooling in small concentrically grouped needles, melting at 95°–97°, and solidifying again at 90°. From ether, which dissolves it freely, it crystallises in large rhombic prisms, acuminate at the summits. Caustic potash slowly decomposes the crystals, even at ordinary temperatures, with formation of bromoform. Sodium abstracts all the bromine from the aqueous solution, part only from the ethereal solution (Klimenko, *J. pr. Chem.* [2]. xiii. 98).

LACTIDE, $C^3H^2O^4$. The formation of this compound from paralactic acid, as well as from ordinary lactic acid, has been already mentioned (p. 1160). L. Henry (*Ber.* vii. 753) finds that its vapour-density is 4.81; consequently its molecular formula must be, not $C^3H^4O^2$ as hitherto supposed, but $C^3H^2O^4$, the vapour-density calculated from the latter formula being 4.96.

By absorption of dry ammonia, lactide is converted into lactamide, $CH^3 \cdot CH(OH) \cdot CO \cdot NH^2$, identical with that (m. p. 74°) which is produced by the action of ammonia on ethyl lactate (iii. 453). Hence it must be regarded as an

ethereal compound, $\begin{smallmatrix} O & O \\ \diagup & \diagdown \\ CO \cdot CH \cdot CH^3 \end{smallmatrix}$, and not as a body which would be at the same

time acid anhydride and alcoholic anhydride, viz. $\begin{smallmatrix} CH^3 \cdot CH \cdot CO \\ O & O \end{smallmatrix}$, since it would then

be converted by ammonia into a diamide, $\begin{smallmatrix} CH^3 \cdot CH \cdot CO \cdot NH^2 \\ O \end{smallmatrix}$, or the correspond-

ing acid ammonium salt, $\begin{smallmatrix} CH^3 \cdot CH \cdot CO \cdot NH^2 \\ O \end{smallmatrix}$.

Lactide melts at 121° (according to Wislicenus at 124.5°; see p. 1160), and boils

under a pressure of 757 mm. at 255° (uncorr.) It is not attacked by acetyl chloride. The temperature at which lactic acid, when subjected to dry distillation, passes into dilactic acid, $C^4H^{10}O^3$, is between 140° and 150°, and that at which this latter compound when heated alone is converted into lactide, is between 200° and 250° (Henry).

LACTIDE BROMAL, syn. with TRIBROMETHYLIDENIC LACTATE (p. 1162).

• **LACTOGLUCOSE**. A constituent of milk-sugar, according to Fudakowski (see SUGARS).

LACTOPHOSPHATES. A pharmaceutical name for mixtures of lactic acid with calcium phosphate. R. Rother (*Pharm. J. Trans.* [3], iii. 570) found that lactic acid saturated with tricalcic phosphate contained 4 mols. of the former to 1 mol. of the latter. The solution, when boiled or left at rest for some time, deposited a precipitate of PO^4CaH :



The formation of this precipitate may be prevented by adding a quantity of lactic acid equal to half that originally present. Directions for the preparation of syrups of calcium lactophosphate are given by Rother (*loc. cit.*), also by Menières a. Langellé (*Pharm. J. Trans.* [3], iv. 142), and for the preparation of cod-liver oil containing calcium lactophosphate by E. Chiles (*ibid.* iii. 785).

LACTUCA. The leaves of the common lettuce (*Lactuca sativa*) fresh and well-developed were found by Church (*Journal of Botany*, March 1876) to contain water, 95.98 per cent.; albuminous matter, 0.71; starch, sugar, gum, 1.68; cellulose and lignose, 0.52; chlorophyll and fat, 0.22; ash, 0.89. This ash was very rich in nitrates.

LACTURAMIC ACID, $C^4H^5N^2O^3 = CH^2.CH(NH.CONH^2).COOH$ (see vol. vii. p. 723).

LACTYL-CARBAMIDE or **LACTYL-UREA**, $C^4H^5N^2O^2 = \begin{matrix} CH^2.CH.NH.CO \\ | \\ CO-NH \end{matrix}$ (*ibid.*)

LANTHANUM. Atomic weight, $La''' = 135.75$ (Marignac); 139.15 (Cleve); 139.2 (Frerichs a. Smith); 139 (Hillebrand).

On the preparation of Lanthanum and its separation from Cerium and Didymium, see CERITE METALS (pp. 421, 422); also DIDYMIUM (p. 642).

A large number of lanthanum salts prepared and examined by Cleve are described under CERITE METALS (pp. 422, 423). The following have been examined by Frerichs a. Smith (*Liebigs Annalen*, xcxi. 355-366); they were prepared in the same manner as the corresponding didymium compounds (p. 642), which, for the most part, they closely resemble.

Platinochloride, $2LaCl^3.3PtCl^4.24H^2O$.—Large orange-coloured very soluble 4-sided plates.

Aurochloride, $2LaCl^3.3AuCl^3.21H^2O$.—Shining plates, very soluble and absorbing moisture from the air, but not deliquescent.

Oxychloride, $LaOCl$.—White, nearly insoluble in water even at the boiling heat. By boiling with an excess of didymium oxychloride suspended in water, it is gradually converted into the soluble chloride, the didymium oxychloride being first resolved into insoluble oxide and soluble chloride, which then gives up its chlorine to the lanthanum and is itself converted into didymium oxide:



Lanthanum and Zinc Bromide, $2LaBr^3.3ZnBr^2.39H^2O$ (or perhaps $36H^2O$).—Resembles the corresponding didymium salt.

Lanthanum and Nickel Bromide, $2LaBr^3.3NiBr^2.18H^2O$.—Exactly resembles the didymium salt.

Lanthanum and Zinc Iodide, $2LaI^3.3ZnI^2.27H^2O$.—Small white very soluble needles; absorbs moisture from the air much more quickly than the corresponding didymium salt.

Lanthanum and Hydrogen Fluoride, $2LaF^3.3HF$.—Thrown down by hydrofluoric or silicofluoric acid from a solution of lanthanum sulphate, as a bulky precipitate, which dries up to a thick white crust.

* Frerichs a. Smith suggest that the precipitate obtained by Cleve on adding hydrofluoric acid to lanthanum acetate, and regarded by him as $2LaF^3.H^2O$ (p. 422), may possibly have been the acid fluoride above described, the hydrogen fluoride of which, given off on heating, may have been mistaken for water of crystallisation.

Lanthanum-zinc Nitrate, $2\text{La}(\text{NO}_3)_3 \cdot 3\text{Zn}(\text{NO}_3)_2 \cdot 69\text{H}_2\text{O}$.—Agrees in properties with the salt prepared by Damour & Deville (*Instil.* 1858, 111), who, however, assigned to it the formula $\text{La}''(\text{NO}_3)_2 \cdot \text{Zn}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ or $2\text{La}'''(\text{NO}_3)_3 \cdot 3\text{Zn}(\text{NO}_3)_2 + 24\text{H}_2\text{O}$.

Lanthanum-nickel Nitrate, $2\text{La}(\text{NO}_3)_3 \cdot 3\text{Ni}(\text{NO}_3)_2 \cdot 36\text{H}_2\text{O}$.—Light green very soluble crystals, which do not absorb moisture from the air so quickly as the corresponding didymium salt.

Lanthanum Hypochlorite, $\text{La}(\text{OCl})_3$.—Chlorine passed into water in which lanthanum hydroxide is suspended, forms after a while a crystalline powder, which redissolves if the stream of chlorine be continued; and on evaporating the filtered solution over the water-bath, the hypochlorite is obtained in easily soluble lustrous plates.

Lanthanum Sulphide, La_2S_3 , obtained by heating the oxide in a current of CS_2 and CO_2 , is a brownish-grey powder which dissolves in acids with evolution of hydrogen sulphide. Cold water decomposes it into lanthanum hydroxide and hydrogen sulphide.

Sulphates.—The normal sulphate, $\text{La}_2(\text{SO}_4)_3$, crystallises from a neutral saturated solution with $6\text{H}_2\text{O}$. On mixing the saturated solution with an equal volume of sulphuric acid and evaporating over the water-bath, fine crystals of the bihydrated salt, $\text{La}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, are obtained.

Basic Sulphate, $[\text{La}_2(\text{OH})_2]_2(\text{SO}_4)_3$.—Hermann obtained this salt by precipitating the normal sulphate with ammonia, as a white bulky precipitate containing water. Frerichs & Smith have obtained it in the anhydrous state.

Selenate, $\text{La}_2(\text{SeO}_4)_3 \cdot 12\text{H}_2\text{O}$.—Colourless prisms, soluble in water. Cleve obtained it with $6\text{H}_2\text{O}$. *Selenite*, $\text{La}_2(\text{SeO}_3)_3 \cdot 9\text{H}_2\text{O}$. Precipitated by alcohol from a concentrated solution of the sulphate mixed with selenious acid. Decomposes as readily as the didymium salts. Cleve's acid selenite (p. 423) was not obtained by Frerichs & Smith.

Phosphates.—The orthophosphate, LaPO_4 , is a colourless gelatinous precipitate formed from lanthanum sulphate and trisodic phosphate. The triphosphate, $(\text{La}_2)_3\text{H}^3(\text{PO}_4)_3$, is formed as a gelatinous precipitate on mixing the solutions of lanthanum sulphate and disodic phosphate. The pyrophosphate, $\text{La}_2\text{H}^2(\text{P}^2\text{O}_7)_3$, is obtained on adding sodium pyrophosphate to lanthanum sulphate, as a colourless precipitate soluble in excess of the sodium salt. Cleve assigns to it the composition $\text{La}_2\text{H}^2\text{P}^2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The metaphosphate, $\text{La}(\text{PO}_3)_3$, is precipitated by sodium metal phosphate from lanthanum sulphate.

Phosphite, $\text{La}_2\text{H}^3(\text{PO}_3)_3$.—Colourless precipitate.

Arsenate, $\text{La}_2\text{H}^3(\text{AsO}_4)_3$, is a colourless gelatinous precipitate; the *arsenite*, $\text{La}_2\text{H}^3(\text{AsO}_3)_3$, is obtained as a crystalline powder by boiling lanthanum hydrate for several hours with aqueous arsenious acid.

Chromate, $\text{La}_2(\text{CrO}_4)_3$.—Obtained, on mixing the solution of neutral potassium chromate and lanthanum sulphate, as a yellow granular precipitate, appearing crystalline under the microscope. Slightly soluble in cold, more readily in hot water, easily in acids.

Manganate, $\text{La}_2(\text{MnO}_4)_3$.—Obtained by heating manganese dioxide (1 pt.) with lanthanum nitrate (4 pts.) for half an hour, then washing the mass with water and drying, as a grey-black powder, insoluble in water, but dissolving with fine rose-red colour in sulphuric acid. The *permanganate*, $\text{La}(\text{MnO}_4)_3 \cdot 21\text{H}_2\text{O}$, is deposited as a brown powder on leaving a solution of potassium permanganate and lanthanum sulphate to itself for about a month.

Borate, $\text{La}_2(\text{B}^3\text{O}_7)_3$.—Gelatinous precipitate which dries up to a transparent brittle crust.

Tungstate, $\text{La}_2(\text{WO}_4)_3$.—Obtained on mixing sodium tungstate with a lanthanum salt as a colourless gelatinous precipitate which dries up over the water-bath to a thick white crust; it is soluble in acids. The *molybdate*, $\text{La}_2\text{H}^2(\text{MoO}_4)_3$, is very much like the tungstate.

The *cyanide* is a gelatinous precipitate which dries up to a dense crust. It unites with other metallic cyanides, forming well-crystallised double cyanides. The *platinocyanide*, $2\text{La}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 \cdot 18\text{H}_2\text{O}$, is obtained, according to Czudnowicz, on adding barium platinocyanide to an excess of lanthanum sulphate.

LANTHANURIC ACID, $\text{C}^3\text{H}^4\text{N}^2\text{O}^3$. See GLYOXYL-CARRAMIDE (p. 890).

LARCH FUNGUS. This fungus, treated with alcohol of 96 per cent., yields a mixture of at least four different resins. The yellowish-white portion, which dissolves with difficulty in cold alcohol, may be separated by digestion with chloroform into two different constituents. (a). The part which is insoluble in chloroform has

the composition $C^{41}H^{70}O^8$, melts at 125° , and dissolves at 14° in 303.8 pts. alcohol of 95 per cent. (β). The part which dissolves in chloroform has the composition $C^6H^{10}O$, melts at 90° , and dissolves in 130 pts. of alcohol.

The portion of the original resin which dissolves easily in alcohol of 95 per cent. has a red colour, and consists of 69.16 per cent. C., 9.44 H., and 21.40 O. It dissolves readily also in alcohol of 75 per cent., and is precipitated therefrom for the most part by water. The constituent which is soluble in water contains 61.91 per cent. C., 8.11 H., and 29.98 O.; it dissolves in 58.8 pts. of alcohol and in 590 pts. of distilled water.

A chemical change appears to be brought about in the resinous mixture by continued boiling with milk of lime, the precipitate thrown down by hydrochloric acid from the filtrate being separable by digestion with chloroform into two different substances. The part insoluble in chloroform has the formula $C^{39}H^{63}O^4$, and dissolves in 165 pts. of alcohol. The constituent which is soluble in chloroform has the composition $C^{35}H^{52}O^6$, and dissolves in 47.8 pts. of alcohol. Both of these bodies contain more carbon than the white resin. On the contrary, the red residue on the filter, which can be separated from the calcium hydrate by hydrochloric acid, and does not pass into the solution, contains a smaller amount of carbon than the red resin of the fungus.

The white resin of the fungus is tasteless. The red resin is, even after the most careful purification, intensely bitter, and is the chief cause of the bitter taste of the fungus. The resin of the Larch fungus contains no constituent which can be converted into sugar by treatment with dilute acid. Umbelliferone occurs among the products of dry distillation of the resin. The resin of the Larch fungus offers considerable resistance to the action of concentrated nitric acid. Among the products of the action of this acid, aided by heat, on the mixture of resins, are found picric acid and succinic acid (E. Masing, *Arch. Pharm.* [3], vi. 111).

LARCH-RED. This substance, obtained by boiling the extract of larch-bark with very dilute sulphuric acid, yields protocatechuic acid when fused with 4 pts. of sodium hydroxide. The same acid may be obtained by similar means, though less advantageously, from the extract itself (Stenhouse, *Chem. Soc. Jour.* xxviii. 7).

LAUREL-WATER. Determinations of the proportion of hydrocyanic acid in laurel-water, prepared from leaves gathered at different seasons, have been made by M. Leger (*Pharm. J. Trans.* [3], iii. 271). 1500 grams of distillate prepared in each of the twelve months of the same year from 1000 grams of leaves were found to contain the following quantities of hydrocyanic acid:

January	76 mgm.	June (old and young leaves)	84 mgm.
February	96 "	July	125 "
March	100 "	August	116 "
April {old leaves	76 "	September	110 "
{buds	100 "	October	116 "
May {old leaves	44 "	November	100 "
{young leaves	110 "	December	66 "

The loss of hydrocyanic acid which laurel-water suffers in keeping is particularly great when it is kept in corked bottles not quite filled.

On Artificial Laurel-water, see A. Ripping (*Arch. Pharm.* [3], ix. 526; *Chem. Soc. Jour.* xxxii. 241).

LAUROCERASIN. This name is given by E. Lehmann (*N. Rep. Pharm.* xxiii. 449) to a substance intermediate in composition between amygdalin and amygdalic acid (i. 201), obtained from the bark of the berry-bearing alder (*Rhamnus frangula*), and the leaves of the cherry-laurel (*Cerasus Laurocerasus*). Rhamnus bark or laurel leaves are exhausted with hot absolute alcohol; and the decoctions, mixed with recently precipitated lead hydroxide, are left to stand for a week, whereby chlorophyll and tannin are thrown down. On subsequently warming the liquid, filtering, and mixing the filtrate with ether, an amorphous precipitate is obtained which may be freed from sugar by boiling with alcohol. Of this substance rhamnus bark yields 0.7, laurel leaves 1.38, per cent. The amorphous product, when freshly precipitated, exhibits the appearance of microscopic granules; they deliquesce very quickly, appear light yellow with a glassy lustre when dried over sulphuric acid, and brownish when dried at 100° ; they are diffusible, optically dextrogyrate, and taste like salicin. Strong sulphuric acid colours them violet, afterwards brownish yellow. They are decomposed by almond-emulsion, but less easily than crystallised amygdalin. When boiled with baryta-water, they yield barium amygdalate and ammonia, of the latter, however, only half as much (reckoned on the dry substance) as is obtainable from the crystallised glucoside. To the product from rhamnus bark Masing assigns the

formula $C^{80}H^{186}N^{20}O^{71} = 2C^{40}H^{93}NO^{23} + 25H^2O$; to that from laurel leaves the formula $C^{80}H^{186}N^{20}O^{60} = 2C^{40}H^{93}NO^{23} + 14H^2O$,—the body, $C^{40}H^{93}NO^{23}$, common to them both, containing the elements of amygdalin, $C^{20}H^{27}NO^{11}$, and amygdalic acid, $C^{20}H^{24}O^{12}$. When the bark or the leaves were simply exhausted with hot alcohol, without the use of lead hydroxide, the same substance was obtained in union with a smaller quantity of water, $2C^{40}H^{93}NO^{23} + 2H^2O$.

LAUROSTEARIN. H. Schiff (*Berl. Ber.* vii. 781) points out that the correction of the older analyses of this substance according to the atomic weights now in use leads to the formula $C^{30}H^{74}O^8 = C^3H^8(O.C^{12}H^{23}O)^3$, instead of the older formula $C^{27}H^{50}O^4$ (iii. 475), so that the fit of the bay-tree, like all other natural glycerin fats, may be regarded as a normal (tri-acid) glycerin-ether—viz. trilauryl-glycerin. The mean of the analyses by Marsson and by Sthamer gives 73.35 per cent. carbon and 11.47 hydrogen, the formula requiring 73.35 C. and 11.60 H.

LAVA. See VOLCANIC PRODUCTS.

LEAD. *Occurrence.*—Native lead is found in the Kirghis Steppe, associated with heavy spar and cerussite in hornstone, and in the gold washings of Katharinon-burg in grains, together with gold, magnetic iron ore, and specular iron ore (v. Kok-scharow, *Jahrb. f. Min.* 1875, 873).

On the occurrence of lead as carbonate, sulphide, &c., see the several compounds.

Desilveration of Raw Lead.—The following method is described by Rozeau (*Dingl. pol. J.* ccxvi. 171). The lead is melted in a pot, skimmed, and then transferred to a second pot, through the bottom of which steam is passed in a fine spray. The steam is blown in with a pressure of 3 atmospheres, and to induce the crystallisation the surface of the bath is sprinkled with water. The oxides thereby formed are skimmed off, and the steam which has passed through the fused metal is condensed in chambers in which the portions of oxide carried with it are at the same time deposited. The melting pot is of course covered, and the lead thrown against the cover must from time to time be removed. As soon as two-thirds of the lead has crystallised out, the still fluid residuum, which is rich in silver, is made to flow through heated tubes into moulds in which it is cast into blocks each weighing half a hundredweight. A fresh quantity of raw lead is then run in from the first pot upon the crystalline mass in the second, and the operation proceeds as before. Lastly the lead crystals are fused in the pot itself, then cast into ingots, and sent into the market.

At the St. Louis les Marseille works a jet of steam is used to stir the fused lead during the Pattinson process. By this the copper is oxidised to black oxide, and antimony is carried away with the stream of vapour; 16 tons of lead are thus worked up in a time in which only 8 to 10 tons could be desilverised by hand labour. The desilverised lead is very soft, and contains only 2 grams of silver in 100 kilograms, whereas the raw lead contains from 1500 to 2000 grams of silver in 100 kilograms (Luce a. Rozan, *Dingl. pol. J.* ccxiv. 238).

At the Clyde Lead-works in Glasgow, a method of desilveration, known as the Flach-Guillem process, is adopted. 18 tons of rich argentiferous lead are melted, 1 per cent. of zinc is added, the molten mass is left to cool, the crust of zinc containing the silver and other foreign metals is removed, and the lead sweated out in a small pot. The lead in the large pot is then treated with another $\frac{1}{2}$ per cent. of zinc in the same way. A third addition of $\frac{1}{4}$ per cent. of zinc suffices to remove the greater part of the remaining silver, 5 dwts. being left in the lead per ton. This lead is then run into the refining pan, and the last traces of zinc are oxidised out.

The zinc and silver alloy is heated in a plumbago crucible having a luted cover, and connected by a plumbago pipe with a cast-iron receiver. The zinc distils over, and is used again. The silver and lead alloy is then cupelled.

All the oxide of lead formed in the operation is reduced in a slag hearth, the fumes being condensed in Johnstone's patent condenser. The lead from the slag hearth, being very impure, has to be treated in a refining pan, by which the impurities are removed. The purified lead is then desilverised as before. Lead by this process can be desilverised in thirty hours with a loss of $1\frac{1}{4}$ per cent. The market lead contains only .0015 per cent. of antimony, and .0004 per cent. of silver (*Engineering*, 1876, September 15; *Dingl. pol. J.* ccxxv. 67).

See further, Roswag a. Geary (*Chem. Centr.* 1878, 367; *Chem. Soc. J.* xxxiv. 819); Kirchhoff (*Dingl. pol. J.* ccxxviii. 265; *Chem. Soc. J.* xxv. 761). On Keith's method of desilveration by electrolysis, see *Dingl. pol. J.* ccxxx. 75, 328; *Chem. Soc. J.* xxxvi. 288, 410.

On the properties of pure lead, and the influence of foreign bodies on its properties and technical utility, see G. Brigel (*Deut. Chem. Ges. Ber.* vi. 191; *Dingl. pol. J.* ccvii. 490).

Hard lead may be prepared by fusing 5 parts of lead with 1 part antimony sulphide, or 2 parts of litharge with 1 part antimony sulphide. The reguli thus obtained consist of lead sulphide and lead antimonide (Brgel).

The presence of bismuth in lead is said to be advantageous in the preparation of white lead by the ordinary Dutch process, the bismuth when intimately mixed with the lead facilitating the oxidation. It often happens, however, that the bismuth accumulates at particular parts of the lead plate, and then withstands oxidation for a considerable time, the plates exhibiting certain unoxidised portions of regular shape, the fractured surface of which is covered with a black coating of metallic bismuth. This effect is probably due to overheating of the lead in melting, the interior of the metal in casting then remaining fluid long enough to allow of the formation of an alloy of lead and bismuth (H. Endemann, *Amer. Chemist*, vi. 457).

Specific Gravity.—The specific gravity of pure lead has been determined by P. Schweizer (*Amer. Chemist*, vii. 174) with the following results:

(1.)	11.352 at 23° = 11.345 at 4°
(2.)	11.366 „ 23° = 11.358 „
(3.)	11.366 „ 18° = 11.356 „

Specimen 1 was taken from the end, 2 and 3 from the middle of an ingot.

Reactions.—1. With Water and Saline Solutions. According to L. Besson (*Compt. rend.* lxxviii. 322), the deposit formed by the action of distilled water and of rain-water on lead and alloys of lead and tin, consists, not of lead carbonate as hitherto supposed, but of a compound containing ammonia, easily recognised on heating the deposit. This result is due to an electrochemical action, whereby ammonia is formed from the elements of air and water.

Mayençon a. Bergeret (*ibid.* 484) find that lead is attacked by all waters, hard as well as soft, a certain quantity of the lead dissolving in the water. According to their experiments, hydrogen sulphide will not detect extremely small quantities of lead in water, because lead sulphide, either precipitated or native, is soluble in soft water, and even in water saturated with hydrogen sulphide. If, however, an electric current be passed through a water containing lead, through which hydrogen sulphide has been passed, metallic lead will be deposited on the platinum wire forming the negative electrode. In this way it has been found that lead is dissolved even by highly calcareous waters, and that it is present in all waters which have passed through lead pipes. The quantity thus dissolved is however too small to exert any deleterious action.

G. Bischof (*Chem. Soc. J.* xxxi. 428) observed that a leaden pipe containing 1.7 per cent. antimony, which passed into a cistern where it was exposed to the alternate action of air and water, according to the variation of the level, became coated with a crust of lead carbonate containing about 4 per cent. of sulphate, whereas a pipe of pure lead exposed to similar influences remained uncorroded. This result shows the danger of using impure lead for the construction of water pipes.

According to Balard (*ibid.* 392), lead is oxidised in contact with water containing air; but if the water contains any salt capable of forming an insoluble compound with this oxide, such a salt will be formed, and the lead will become covered with a closely adhering crust which stops all further action. If, on the contrary, no such salt is present, the action will go on without interruption.

According to Bobierre and Belgrand (*Compt. rend.* lxxviii. 317), lead pipes constantly filled with drinking water are not attacked by it. Distilled water, holding in solution calcium sulphate or bicarbonate, or sodium phosphate, borate, carbonate, or bicarbonate, does not act on lead, whereas potassium nitrate, calcium chloride, barium chloride, sodium acetate, and sodium formate do not interfere with the action of distilled water on lead.

The following observations on the influence of various salts on the solvent action of water on lead, have been made by M. M. P. Muir (*Chem. News*, xxxiii. 102, 125, 145; xxxiv. 223, 234). *Nitrates* when alone, even when present in small quantity only, increase the solubility of lead in water to a very considerable extent. The presence of other salts, however, such as sulphates, carbonates, and chlorides, greatly diminishes this solvent influence of the nitrates, and sometimes destroys it altogether; the action of carbonates in this way is especially favourable. *Sulphates, carbonates, and chlorides*, added to distilled water, likewise diminish its solvent action on lead, a small quantity of either of these salts producing even a better effect than a larger quantity. In presence of those salts which exert a retarding action, the quantity of lead dissolved scarcely exhibits any further increase after the lapse of twenty-four hours, whereas in the case of salts which, like the nitrate, increase the solubility, the amount dissolved increases continuously with the duration of the action. Water

saturated with carbonic acid under ordinary pressure does not exert much solvent action on lead, but water saturated with carbonic acid under a pressure of 6 atmospheres dissolves lead in considerable quantity. The solubility is not increased by the presence of a small quantity of ammonium nitrate, and potassium carbonate exerts a retarding influence in this case also; but the quantity of lead dissolved is still so considerable as to render such water unfit for drinking.

The precipitate formed on the surface of exposed lead, or deposited at the bottom of the vessels, consists of hydrated basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. The solubility of this salt in the saline solution is increased when access of air is prevented; addition of carbonic acid increases the solubility. A solution of potassium carbonate does not exert any solvent action on lead hydrocarbonate. The action of the air gives rise to a slow separation of the dissolved hydrocarbonate, which is slowest from the solution in ammonium nitrate. The order of solubility of lead hydrocarbonate in various saline solutions, agrees nearly with that of metallic lead in the same liquids. The following table shows the numerical results, which, however, must be regarded as only approximate.

Solubility of Lead Hydrocarbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, in various dilute Saline Solutions at ordinary temperatures.

Solution.	Grams of salt per litre.	Solubility of lead salt.	
		Experiments carried out in corked flasks.	Experiments in beakers.
Ammonium sulphate . . .	0.20	1 part in 32,000	1 part in 43,000
Potassium nitrate . . .	0.20	1 " 26,000	1 " 43,000
Calcium chloride . . .	0.20	1 " 23,000	1 " 26,000
Ammonium nitrate . . .	0.20	1 " 4,600	1 " 26,000
Water saturated with CO_2 .		1 " 4,300	1 " 4,300

(Muir, *Chem. Soc. J.* xxxi. 660).

On the action of potable waters and of saline solutions on lead, see also Fordos (*Compt. rend.* lxxvii. 1099; *Chem. Soc. J.* xxvii. 232; *Compt. rend.* lxxviii. 1208; *Chem. Soc. J.* xxvii. 872; *Jahresb. f. Chem.* 1874, 278).

According to J. Merrick (*Amer. Chemist*, iv. 289) lead is strongly acted upon by oil of turpentine.

On the action of nitric acid on lead, see NITRIC ACID.

Detection of Lead.—H. B. Cornwall (*Chem. News*, xxxiv. 27) recommends for this purpose the use of v. Kobell's test for bismuth, which consists in heating the substance under examination on charcoal, with a mixture of sulphur and potassium iodide (vii. 190), whereby a yellow sublimate of lead iodide is obtained. The great volatility of this compound renders it possible to detect lead by this reaction, even in presence of bismuth and other metals.

E. Klingelhöffer (*N. Jahrb. Pharm.* xxxix. 86) has observed the presence of lead in many commercial samples of tartaric acid. To detect it, the acid must be neutralised with ammonia before precipitating with hydrogen sulphide.

The presence of lead in tinned vessels may be detected by laying on the thickest part of the tinning a drop of nitric acid, removing the acid by gentle heating, and after the metal has cooled, laying on the pulverulent spot a small quantity of a dilute solution of potassium iodide. This solution is without action on stannic oxide, but it acts on lead nitrate, producing a yellow precipitate of lead iodide. The reaction is very delicate, giving a distinct yellow coloration even with only 1 per cent. of lead (Fordos, *Bull. Soc. Chim.* [2], xxiii. 346). With regard to this method, Pürckhauer observes that the nitric acid cannot be completely expelled by mere warming, and that consequently tin even quite free from lead will, when treated as above, exhibit a more or less distinct yellow coloration due to iodine separated by the still remaining acid. He therefore recommends that, previous to the addition of the potassium iodide solution, the spot be wetted with a very weak solution of potash. A similar process for the detection of lead in tinned vessels is given by A. Bobierre (*Compt. rend.* lxxx. 961), who, however, uses glacial acetic acid instead of nitric acid.

Estimation. 1. By *Electrolysis*.—Lead may be precipitated electrolytically in a coherent state and of a dull colour by operating on solutions, preferably alkaline, containing phosphoric and tartaric acids. The presence of acetic acid tends to keep the positive pole free from peroxide (Pardo a. Mascazzini, *Gazz. chim. ital.* vii. 223). See also Riche (*Compt. rend.* lxxxv. 226).

2. As *Iodate*.—Lead may be estimated as iodate in the absence of hydrochloric acid, or alkaline chlorides, bromides, or iodides, lead iodate being much less soluble in alcohol even than the sulphate. The lead iodate may be weighed, or it may be pre-

precipitated with a standard solution of iodic acid, the excess of which is estimated in the filtrate. The iodate solution must be standardised by means of a solution of pure lead nitrate. Hydrochloric acid rapidly dissolves lead iodate (C. Cameron, *Chem. News*, xxviii. 145).

Volumetric Estimation by Chromic Acid.—The lead salt dissolved in water is mixed with a little acetic acid, and excess of a standard chromate solution containing 14.761 grams of potassium dichromate per litre; the lead chromate is filtered off, and the excess of potassium dichromate is determined by acidulating with hydrochloric acid, and running in a solution of stannous chloride till the chromic acid is nearly but not entirely reduced. A few drops of starch paste and potassium iodide are then added, and stannous chloride cautiously poured in till the blue colour of the iodide of starch disappears (C. W. Hinman, *Am. J. Sci.* [3], xiv. 478). Pellet (*Bull. Soc. Chim.* [2], xxii. 246) adopts a similar process, but estimates the excess of dichromate by addition of a ferrous salt and titration with permanganate.

Estimation of traces of Lead in Waters.—The colorimetric estimation of traces of lead in waters by passing hydrogen sulphide into the liquid yields very low results in presence of free hydrochloric or even of free acetic acid; indeed, traces of lead are frequently not converted into sulphide at all under these conditions. G. Bischof modifies the process by dissolving the water-residue, after it has been gently ignited, in a little hydrochloric acid as possible, filtering, and passing hydrogen sulphide for a short time through the filtrate and washings. The liquid is then mixed with a slight excess of ammonia, and again with excess of pure hydrochloric acid. The formation of ammonium sulphide in the liquid secures the conversion of all the lead present into sulphide, which then remains unchanged on again acidifying. In some cases it is preferable to unite the lead sulphide precipitate into lumps by shaking the liquid; filter this off; dissolve it in pure strong hydrochloric acid; and reprecipitate it as described above for the colorimetric estimation. This proceeding has the advantage of distinguishing lead sulphide from copper sulphide, the latter not dissolving in strong cold hydrochloric acid at all. The standard solution used for comparison is diluted if necessary in the test-glass until its colour intensity is the same as that of the test sample. Shaking of the solution after passing the hydrogen sulphide must be avoided, as the colour intensity is apt to be altered by the precipitate uniting into flakes (*Zeitschr. anal. Chem.* 1879, 73).

Assay of Lead Ores.—The following method is described by Mascazzini (*Dingl. pol. J.* ccvii. 46). Pure ores are reduced with zinc and hydrochloric acid, and the metallic lead, after being separated by washing, is fused with an appropriate flux. Impure ores, containing zinc blende, copper pyrites, or iron pyrites, must first be gradually heated to redness with ammonium sulphate in order to convert the sulphides into sulphates. On subsequent treatment with sulphuric and hydrochloric acid, the lead remains as sulphate, the silver as chloride, and these compounds may be reduced with zinc, and the metals fused as above described. As a flux for fusing the spongy lead, Mascazzini recommends that proposed by Plattner, viz. 13 parts potassium carbonate, 10 sodium carbonate, 5 fused borax, and 5 dry starch. The same process may serve for the assay of lead ores rich in gold and silver, and, with certain modifications, for the valuation of antimony, tin, and copper ores.

To give greater exactness to the estimation of lead in sulphuretted ores, J. Löwe (*Dingl. pol. J.* ccix. 139), after treating the ore with nitric acid, whereby a residue is left containing more or less lead sulphate, exhausts this residue further with sodium thiosulphate, precipitates the lead thereby dissolved with hydrogen sulphide or ammonium sulphide, and converts the precipitated lead sulphide into sulphate. The amount of lead calculated therefrom is then added to the principal quantity contained in the nitric acid solution.

According to F. Mohr (*Zeitschr. anal. Chem.* 1873, 142) the decomposition of galena which Storer effects by the action of hydrochloric acid and zinc (vii. 727), may also be effected by the use of hydrochloric acid alone; and the separation of the lead in the metallic state, according to Storer's method, may take place even when the zinc is not in direct contact with the lead sulphide. The weighing of the lead in this metallic state is less exact, according to Mohr, than its estimation as sulphate or as oxalate, which latter salt is quite insoluble in excess of oxalic acid, and may be titrated with permanganate.

When galena is triturated with a solution of acid potassium sulphate, a brisk evolution of hydrogen sulphide takes place, whereas other sulphuretted minerals, with the exception of zinc-blende, do not exhibit this reaction. Acid potassium sulphate may therefore serve as a test for the recognition of galena in mixed ores (Jannettaz, *Compt. rend.* lxxvii. 838).

Lead Alloys. 1. With Antimony. The action of hydrochloric acid on alloys

of lead and antimony has been examined by H. v. d. Planitz (*Deut. Chem. Ges. Ber.* vii. 1664). The alloys used in the experiments were formed by melting very soft lead with quantities of antimony such that the alloys contained 0.5, 1, 2, 5, 10 and 20 per cent. of antimony. They were cast in the form of rectangular plates, 6 c.m. long, 2.5 broad, and 0.25 thick. In one series of experiments the plates were completely immersed in the acid, in another series only partially, so that they were partly in contact with the air. As soon as these plates were immersed in pure strong hydrochloric acid, evolution of gas began, slow with pure lead, quicker with the alloys in proportion to the quantity of antimony contained in them. The hydrogen evolved in the action of the acid on antimonietted lead contained hydrogen antimonide. After the action had continued for eight to fourteen days, a split showed itself on each edge of the plate and continually grew wider, and from the four narrowest faces of the plate four prisms separated, this effect in the case of the 20 per cent. alloy taking place after about 3 weeks. At the same time the rest of the alloy became considerably thicker, and altered in appearance, the surface becoming covered with shining scales of lead chloride. If the plates were left in the acid still longer, they ultimately split in halves, in the direction of the cleavage-face passing through the edges which were formed by the division of the prisms in the middle of the thickness of the original plates. In the alloy richest in antimony this division took place a week after the separation of the prisms. The plates had become rotten and even friable, and were penetrated throughout by chloride of lead. The same series of changes took place in the less highly antimonietted alloys, but more slowly, and in pure lead the action was scarcely perceptible. When, however, the plates were partly in contact with the air, the formation of lead chloride was facilitated, and a commencement of division was distinctly observed after some months, even in the case of pure lead.

2. With Bismuth. A case of spontaneous decomposition in an alloy of lead and bismuth is described by A. Vogel (*N. Rep. Pharm.* xxii. 471). Some castings of this alloy, of dark, nearly black colour, were covered on some points with excrescences due to oxidation, and on others the alteration had proceeded so far that the metal could be rubbed to a coarse powder between the fingers. At the same time the casting had lost its flat shape, and was curved to one side. The fresh fracture, when examined under the microscope, exhibited a grey colour, dotted here and there with metallicallly lustrous spangles. In every case the decomposition had commenced at one point, and spread therefrom as a centre through the entire mass. The analysis of three of these castings gave: (1). Lead 66, bismuth 34; (2). Lead 86, bismuth 14; (3). Lead 88, bismuth 12. The powder dissolved partially (20 to 30 per cent.) in acetic acid, with brisk evolution of carbon dioxide, yielding a solution containing bismuth as well as lead. The decomposition may perhaps be attributed to the well known tendency of bismuth to assume the crystalline form.

On the action of Water on Alloys of Lead and Tin, see p. 1167.

On Lead-amalgam. See MERCURY.

Lead Chloride, $PbCl_2$. Roscoe (*Ber.* xi. 1196) has determined the vapour-density of this compound by heating it to bright redness in a long-necked porcelain globe. The following results were obtained:

Temperature	1046°	1089°	1077°	1070°
Specific gravity of vapour. . .	9.12	9.72	9.51	9.54

showing that the molecular formula of the compound is $PbCl_2$, which gives for the calculated vapour-density the number 9.62.

Formation of Horn-lead in Historic Times.—This mineral has been found at Bourbonne-les-Bains, in prismatic crystals and thick crusts, coating two leaden pipes of Roman workmanship. One of these pipes is internally corroded even to perforation; the other encloses a bronze pipe—doubtless a repair rendered necessary by the corrosion of the latter. The bronze is coated on the inside with a layer of atacamite. Outside the crust of horn-lead is a coating of galena mixed with gypsum (Daubrée, *Compt. rend.* lxxxi. 182).

Oxysalts. Carbonate.—On the occurrence and crystalline form of the native carbonate, see CERUSSITE (p. 425). On the formation of the crystallised carbonate on some objects found at Pompeii, and on the solubility of the salt in ammonium butyrate, see CARBONATES (p. 412). On the decomposition of lead carbonate by sodium oxalate and of lead oxalate by sodium carbonate, see CARBONATES (p. 410).

On the Preparation of White Lead, see K. v. Weise (*Dingl. pol. J.* cccviii. 434; *Chem. Soc. Jour.* xxvi. 1268); Wittstein (*Dingl.* ccxii. 223; *Jahresh. f. Chem.* 1874, 1110); W. Hampe (*Am. Chem.* v. 241; *Jahresh. f. Chem.* 1875, 1074).

Sulphate.—Crystals of lead sulphate (anglesite) from the White Rose vein of

the Eleonora Mine at Langenstriege in Saxony, are described by A. Frenzel (*Jahrb. f. Min.* 1874, 684). They occur in three types: horizontally prismatic ($4P \infty . \infty P$), pyramidal ($P . 2P$, sometimes also ∞P), and upright prismatic ($\infty P . \infty P2 . \infty P \infty . P \infty . 0P$). Crystals of anglesite with numerous faces from the Hüttenberg mining district in Carinthia are described by v. Zepharovich (*Verh. geol. Reichsanst.* 1875, 76).

Sulphato-carbonate.—According to Laspeyres there are two distinct native sulphato-carbonates of lead, one anhydrous (leadhillite), the other hydrated (maxite): see vii. 732, 782; also MAXITE in this volume. Bertrand, on the other hand, regards maxite, not as a distinct mineral species, but as leadhillite altered by the action of water; and later experiments by C. Hinze (*Pogg. Ann.* clii. 256; *Jahrb. f. Min.* 1874, 974) point to the conclusion that the two minerals are identical, their composition being represented by the formula $2PbSO^4.4PbCO^3.2H^2O$. Both minerals when heated give off no water at 100° and only about 0.1 per cent. at 200° ; by prolonged heating, however, the following quantities of water—substantially the same for both—were obtained:

	1 h.	5 h.	10 h.	15 h.	20 h.
Leadhillite (Scotland).	0.489	0.848	0.978	1.346	1.735
Maxite (Sardinia)	0.445	0.850	0.966	1.353	1.739

The optical characters were also found to be identical. An analysis of maxite gave the values A, agreeing very nearly with those calculated from the formula above given, B:

	PbO	SO ³	CO ²	H ² O	Sp. gr.
A.	80.80	8.17	9.18	2.00 = 100.15	6.547 at 18.9°
B.	80.76	8.27	9.11	1.86 = 100	

Tellurate of Lead. See TELLURIUM.

Sulphide, PbS. On the occurrence of galena in rods (so-called *Röhrenerze*) at Raibl, see Posepny (*Jahresb. f. Chem.* 1873, 1146). On the crystallography of galena, see Sadebeck (*Zeitsch. geol. Ges.* xxvi. 617; *Jahrb. f. Min.* 1875, 83). On the occurrence of galena together with lead sulphate as an incrustation at Bourbonne-les-Bains, see p. 1170. On the decomposition of galena by zinc and hydrochloric acid, and by acid potassium sulphate, see p. 1169.

LEAD-CHAMBER CRYSTALS. See NITROSULPHONIC ACID.

LEADHILLITE. (*vid. sup.*)

LEAVES. See PLANTS.

LECANORA. The ethereal extract of *Lecanora atra*, collected in the neighbourhood of Palermo, yielded, on evaporation, a crystalline mass mixed with a soft brown resin, easily removed by washing with cold ether. The crystals are a mixture of two acids, which were separated by means of chloroform; one (*atranoric acid*) is colourless, and but slightly soluble in cold chloroform; whilst the other, which is yellow, is very soluble.

Atranoric acid crystallises from chloroform in small, colourless, transparent prisms, which melt at 190° , and are but very slightly soluble in cold alcohol or ether; it is moderately soluble in boiling chloroform. The results of its analysis correspond closely with the formula $C^{10}H^{18}O^8$. It has feeble acid characters, although it does not affect litmus, dissolving in alkaline solutions, and being reprecipitated by acids. Boiled with aniline and alcohol, it yields a compound crystallising in lustrous yellow needles, which melt at 156° . Heated with alcohol at 150° , it is converted into a crystalline substance, very soluble in alcohol. It forms long needles, which melt at 115° .

The yellow acid accompanying atranoric acid in this lichen, closely resembles usnic acid in appearance, general characters, and behaviour with solvents, but melts at 175° , whilst usnic acid melts at 195° – 197° . Heated with alcohol to 150° , it yields a substance crystallising in slender needles, and melting at 175° just like the decarbusnic acid obtained from usnic acid by this process. With aniline and alcohol it also behaves like usnic acid. The product of the dry distillation of the acid, when extracted with water and filtered from tar, gives a yellow colour with ammonia and potash, brown with ferric chloride, and deep red with sodic hypochlorite. Usnic acid (from *Zeora zordida*) gives results almost identical. This would tend to show that the acid is merely usnic acid whose melting point is lowered by the presence of some impurity in small quantity; the results of the analysis give carbon about 0.5 per cent. lower than that required by the formula $C^{10}H^{18}O^8$. It is perhaps the betausnic acid of Hesse; and the cladonic acid of Stanhouse, extracted from *Cladonia rangiferina*, may be merely impure usnic acid (Paternò a. Ogialoro, *Gazz. chem. ital.* 1877, 189).

LEDUM OIL. The volatile oil of the Marsh Wild Rosemary (*Ledum palustre*), when recently prepared, is yellowish, viscid, lighter than water, and has a pungent odour. When exposed to the air, the greater part of it solidifies to a crystalline mass soluble in alcohol. The fresh oil, when kept in closed vessels, gradually becomes thicker and finally solidifies to a gelatinous mass, which dissolves in alcohol and ether, and solidifies in large prisms when the solvent is evaporated. Chlorine, bromine, and iodine act strongly on the solidified oil (*Ledum camphor*); sulphuric acid dissolves it, forming a colourless liquid which is turned violet by nitric acid. The analysis of *Ledum camphor* leads to the formula $C^{28}H^{48}O$ (J. Trapp, *Russ. Zeitschr. Pharm.* 1874, 289; compare iii. 567).

N. Iwanow (*ibid.* 1876, 577) prepared *Ledum* oil from the plant growing in the neighbourhood of St. Petersburg, by distillation with water. The largest yield, consisting of a white crystalline mass saturated with oil, was obtained from the leaves and young twigs before flowering. By repeated crystallisation from alcohol, colourless prisms were obtained, having a faint odour, insoluble in water, but easily soluble in alcohol, ether, chloroform, and benzene; they melt at 101° to a liquid which boils at 174° ; their alcoholic solution is dextrogyrate. Their analysis led to the formula $C^{28}H^{48}O^2$. The oil which remained in the alcoholic mother-liquor yielded, on prolonged standing, another crop of crystals; the rest of the oil was not further examined. The aqueous distillate of the plant yielded, on agitation with ether, a mobile, yellowish-red, fragrant oil having the composition $C^{28}H^{48}O$.

LEGUMIN. See PROTEIDS.

LEGUMINOSE. On the detection of the flour of leguminous seeds in wheat-flour, see p. 792.

LEMON-JUICE. *Adulteration with Nitric Acid.*—This acid, which has recently come into use as an adulterant of lemon-juice, to increase its acidity, converts the citric acid of the juice, wholly or partially, during the process of concentration by heat, into oxalic, acetic, and carbonic acids, so that, on neutralising the juice with milk of lime, there is obtained, instead of citrate, a mixture of oxalate, acetate, and carbonate of calcium. The nitric acid may be detected by adding to a small quantity of the juice in a test-tube, an aqueous solution of ferrous chloride strongly acidulated with pure hydrochloric acid and quite free from ferric salt; boiling the liquid for a few minutes; and testing it with potassium thiocyanate dissolved in water. If the liquid contains nitric acid, it will be coloured more or less deeply red, according to the quantity of ferric thiocyanate thus produced.

This process succeeds equally well if the juice likewise contains common salt, sulphuric acid, or tartaric acid. To apply it to boiled lemon-juice, the juice must be diluted with water in order that the colour produced by the thiocyanate may be distinctly visible (Scribani, *Gazz. chim. ital.* 1878, 284).

On the estimation of Citric Acid in Lemon-juice, see CITRIC ACID (p. 507).

LEMON-OIL. See TERPENES.

LEONHARDITE (iii. 571). Crystals of this mineral from Floitenthal are described by Brezina (*Jahrb. f. Min.* 1877, 644); they are from 1 to 4 cm. long, and exhibit the combination $\infty P. 0P$. They have been analysed by A. Smita (*ibid.* 1878, 81), who found for the ignited substance the values given under A, agreeing nearly with the formula, $CaAl^2Si^4O^{12}$ or $CaO.Al^2O^3.4SiO^2$; (B) and for the substance heated over sulphuric acid till its weight became constant, the values C, leading to the formula $H^4CaAl^2Si^4O^{14}$ or $CaO.Al^2O^3.4SiO^2.3H^2O$ (D):

	SiO^2	Al^2O^3	CaO	H^2O	
A found. . . .	60.15	25.91	14.19	—	= 100.25
B calc.	60.18	25.78	14.04	—	= 100
C found.	52.92	22.44	12.23	12.38	= 99.97
D calc.	53.00	22.70	12.37	11.93	= 100

Rammelsberg regards leonhardite as a laumontite (iii. 472) which has lost a molecule of water, and this view is confirmed by the experiments of Smita. Laumontite has the composition $H^4CaAl^2Si^4O^{14} + 2aq.$, and of its two molecules of crystallisation-water, one is given off slowly in dry air at ordinary temperatures, quickly at 100° , while the second requires a heat of 300° to expel it. The remainder of the water ($2H^2O$) is given off only at a red heat, and must be regarded as so-called water of constitution. Leonhardite is a laumontite which has lost about half the first molecule of crystallisation-water belonging to the latter, and therefore contains a quantity of water rather greater than that required by the formula $H^4CaAl^2Si^4O^{14}$ or $H^4CaAl^2Si^4O^{14} + aq.$, which, however, correctly represents its composition after it has been exposed for some time to dry air, or heated to 100° .

LEPIDIN, $C^{22}H^{20}O$ (also called *Lepidene*). This compound, discovered by Zinin in 1867, is formed, together with dibenzyl and an oily body, by heating benzoin with fuming hydrochloric acid, and is separated from the other products by its sparing solubility in alcohol and ether. It crystallises from alcohol or acetic acid in feathery or laminar groups of flat needles, melts at a little above 175° , and boils at 220° . It is insoluble in water, soluble in 170 pts. of boiling alcohol, nearly insoluble in cold alcohol, soluble in 38 pts. of boiling and 92 pts. of cold ether, in 28 pts. of boiling and 500 pts. of cold glacial acetic acid (vi. 780). According to a later determination by Zinin (*Bull. Soc. Chim.* [2], xxv. 292) it dissolves at the boiling heat in 16 pts. of acetic acid of sp. gr. 1.0659.

Dibromolepidin, $C^{22}H^{18}Br_2O$, obtained by adding bromine to lepidin dissolved in acetic acid, forms needle-shaped crystals melting at 190° (vi. 781).

Chlorolepidins. The action of chlorine on lepidin dissolved in acetic acid is different from that of bromine, giving rise not to dichlorolepidin, but to needle-shaped oxylepidin (*infra*).

Dichlorolepidin, $C^{22}H^{18}Cl_2O$, is known in two modifications: (a). Lepidin heated with an equal weight of phosphorus pentachloride till all excess of the latter is distilled off, is converted into a resin, the solution of which in ether or in boiling acetic acid deposits crystals having the composition of dichlorolepidin, soluble in 66 parts of boiling alcohol, and melting at 169° . (B). The sparingly soluble modification of dichloroxylepidin (*infra*), boiled with zinc and acetic acid, dissolves readily, forming a solution which, when poured into water, yields a curdy precipitate, consisting of a mixture of two substances, one easily soluble in ether, the other insoluble; and on evaporating the solution obtained by treating this precipitate with ether, and recrystallising the residue from acetic acid, or better from alcohol, long, rather thick, white needles are obtained, consisting of an isomeric dichlorolepidin, which dissolves in 12.5 parts of boiling acetic acid, in 17.4 parts of boiling alcohol, and melts at 166° (Zinin, *Deut. Chem. Ges. Ber.* v. 1104; *N. Petersb. Acad. Bull.* xx. 547).

The higher chlorolepidins are obtained by heating oxylepidin in sealed tubes with pentachloride or oxychloride of phosphorus. $C^{22}H^{18}Cl_3O$ forms white crystals melting at 186° . $C^{22}H^{14}Cl_6O$ and $C^{22}H^{12}Cl_8O$ are amorphous, the former melting at 80° – 90° , the latter softening at 70° and melting at 97° (vi. 781).

Oxylepidin, $C^{22}H^{20}O^2$, formed by the action of nitric acid on a boiling solution of lepidin in glacial acetic acid, was originally obtained in yellow needles melting at 220° (vi. 781). Subsequent experiments by Zinin (*Deut. Chem. Ges. Ber.* v. 1104) have shown that it is susceptible of three modifications. When the compound obtained in the manner just mentioned is heated to 340° (slight evolution of gas then taking place), it solidifies on cooling to a resinous mass which dissolves in 8 to 10 parts of ether, and the solution yields on evaporation three kinds of crystals, viz. tablets, short four-sided prisms, and microscopic octohedrons.

Tabular oxylepidin crystallises in rhombs sometimes 10 mm. long. It dissolves in 4.5 parts of boiling alcohol of 95 per cent., and the solution may be concentrated to the strength of 1 in 45, whereupon the liquid boils up and solidifies completely. This variety of oxylepidin dissolves in 1 part of acetic acid. It may be heated to 130° without loss of weight, melts at 136° , and solidifies to an amorphous resin. Zinc does not act on its solution in acetic acid. When 20 grams of tabular oxylepidin are dissolved in a solution of 5 grams of potassium hydroxide in 40 grams of alcohol, a potassium salt is formed belonging to an acid $C^{22}H^{22}O^2$, which is insoluble in water, but dissolves in 3.5 parts of boiling alcohol, readily in ether, and separates from the boiling solutions of its salts, on acidulation, in the form of a soft resin. This acid crystallises in four-sided prisms or in hemispherical groups, and melts at 196° , with loss of water, leaving a residue of tabular oxylepidin (Zinin, *Ber.* v. 1104).

Octohedral oxylepidin, besides being formed, together with the other two modifications, in the manner above mentioned, is likewise produced by boiling the needle-shaped variety with alcoholic potash or soda. To prepare it, 20 parts of needle-shaped oxylepidin are heated in a reflux apparatus with 300 parts of 95 per cent. alcohol and about 15 parts caustic soda, till the crystalline mass, which has become granular, no longer exhibits any needles when examined by the microscope (12 to 15 hours). Should the liquid, which is usually light yellow, assume a dark brown colour during the boiling, it must be poured off from the deposit, and the latter, after washing with alcohol, boiled with a fresh portion of alcoholic soda solution. 20 grams of needle-shaped oxylepidin yield about 15 grams of the octohedral modification, which may be purified by washing with alcohol, water, and ether, and recrystallisation from acetic acid. Octohedral oxylepidin is very slightly soluble in boiling alcohol, and dissolves in 76 parts of boiling acetic acid. It melts at 232° to a liquid, which

solidifies again in the crystalline form at 200° . It is not acted on by boiling alcoholic potash.

By dry distillation all the three oxylepidins are converted into a body which may be purified by washing with a small quantity of ether, treatment with alcoholic potash, and recrystallisation from alcohol. This substance dissolves in 18 parts of boiling and 266 parts of cold 95 per cent. alcohol, and crystallises in four-sided plates which may be heated to 130° without loss of weight, and melt at 150° . It agrees in composition with the formula $C^{28}H^{20}O$, and is therefore isomeric with lepidin.

Dibromoxylepidin, $C^{28}H^{18}Br^2O^2$, is known in four modifications. One of them, which crystallises in needles, is obtained by adding bromine in excess, but by small portions, to a boiling solution of needle-shaped oxylepidin in glacial acetic acid. Another modification is produced by treating needle-shaped oxylepidin with bromine not in excess, also by the action of nitric acid on dibromolepidin dissolved in glacial acetic acid. It melts at 222° , dissolves in 40 parts of boiling acetic acid, and separates therefrom on cooling in the form of a radiate crystalline mass. When heated above its melting point, it is converted into a resinous substance, easily separable into two dibromoxylepidins isomeric with the preceding, and analogous to the two dichloroxylepidins produced in a similar manner (*infra*). One of them is very sparingly soluble, whilst the other is a resinous substance easily soluble in alcohol, ether, and glacial acetic acid, and converted by alcoholic potash into dibromoxylepidinic acid, which is monobasic, dissolves in boiling acetic acid, and crystallises therefrom on cooling in six-sided laminæ.

The sparingly soluble modification is also produced by heating needle-shaped dibromoxylepidin with a quantity of alcoholic potash not sufficient to dissolve it completely: it is nearly insoluble in ether; a mixture of 66 parts acetic acid and 1000 parts boiling alcohol of 95 per cent. dissolves it partially, and the solution on cooling deposits it in rather thick, lemon-yellow rhombic plates, which melt at 239° , and are converted at a higher temperature into the resinous modification. Needle-shaped dibromoxylepidin, or its sparingly soluble isomeric, dissolved in 12 parts of acetic acid and subjected to the action of zinc, is converted into a mixture of dibromolepidin (m. p. 190°) and hydrodibromoxylepidin, $C^{28}H^{20}Br^2O^2$, which may be separated by precipitating them with water, drying the crude mass, and treating it with ether in which the dibromolepidin is very easily soluble. Needle-shaped dibromoxylepidin moistened with alcohol and treated with sodium-amalgam, and the sparingly soluble modification subjected to the action of zinc and acetic acid, behave like the corresponding dichloroxylepidins when similarly treated (Zinin, *N. Petersb. Bull.* xxi. 66).

Chloroxylepidins. *Monochloroxylepidin*, $C^{28}H^{19}ClO^2$, is formed by heating 2 parts tabular oxylepidin, 2 parts phosphorus pentachloride, and 1 part phosphorus oxychloride to 180° – 200° for 12 hours, and remains, on treating the product with water and 4 or 5 vols. ether, as a white powder, which, after crystallisation from boiling acetic acid (1 part dissolving in 22.8 parts of the acid), resembles tetrachlorobenzile in appearance and solubility. It melts without loss of weight at 185° (Zinin, *Ber.* v. 1104).

Dichloroxylepidin, $C^{28}H^{18}Cl^2O^2$, like the corresponding bromine-compound, is known in several modifications. One of these is prepared by heating 1 part lepidin with 4 or 5 parts phosphorus pentachloride to 115° – 120° till the whole is dissolved, pouring the hot product, which solidifies on cooling, into water, and washing the precipitate with ether; also by the action of oxidising agents on needle-shaped dichlorolepidin.* It forms small needles, which melt without loss of weight at 20.2° , and dissolves in 90 parts boiling ether, in 13.7 parts boiling and 146 parts cold acetic acid (Zinin, *loc. cit.*); according to a later determination (*N. Petersb. Acad. Bull.* xxi. 66) it dissolves in 16.8 parts boiling acetic acid of sp. gr. 1.0659. When dissolved in acetic acid (1 part in 7) and boiled with zinc, it is converted into a mixture of dichlorolepidin (60 per cent.) and hydrodichloroxylepidin, $C^{28}H^{20}Cl^2O^2$ (16 per cent.), separable by ether, in which dichlorolepidin dissolves with great facility.

When this needle-shaped dichloroxylepidin is heated nearly to its boiling point, it is converted into two isomeric modifications, one of which is very soluble in alcohol, ether, and acetic acid, separates from its solutions in the form of a soft resin, and reacts with alcoholic potash, similarly to tabular oxylepidin (p. 1173), yielding a monobasic acid, viz. dichloroxylepidinic acid, $C^{28}H^{20}Cl^2O^3$ (p. 1175). The portion of the overheated dichloroxylepidin which is insoluble in ether (3 to 4 per cent. of the whole) is also a dichloroxylepidin, and is analogous in its characters to octohedral oxylepidin. When heated to commencing ebullition, it is converted into the easily soluble modification which yields dichloroxylepidinic acid. This modification, called by Zinin 'sparingly soluble dichloroxylepidin,' is also produced in large quantity by

the action of alcoholic potash or soda on needle-shaped dichloroxyepid. To prepare it, a mixture of 20 grams needle-shaped dichloroxyepid, 200 alcohol and 15 sodium hydroxide is heated (for 20 to 24 hours) till the sediment, when examined by the microscope, appears free from needle-shaped dichloroxyepid; the product amounts to 16 grams. It forms a granular powder, the individual grains of which appear under the microscope as groups of short thick four-sided prisms. It melts at 230° , is nearly insoluble in alcohol and in ether, and dissolves in 36 parts of boiling acetic acid, the solution on cooling retaining only 2 per cent. of the substance. It is identical with the modification obtained in small quantity by the action of heat on needle-shaped dichloroxyepid.

Dichloroxyepidinic acid, $C^{28}H^{20}Cl^2O^2$.—When dichloroxyepid heated above its melting point is treated with ether and the ether left to evaporate, the remaining resinous mass dissolved in boiling alcohol containing a little caustic potash, the solution largely diluted with water, and the filtered liquid mixed with acetic acid, a yellowish resin is precipitated which becomes hard and brittle on cooling. On pulverising it and adding a little acetic acid, the powder softens and partly dissolves, and suddenly there is formed a compact brittle mass, which is to be pulverised and washed with small quantities of cold acetic acid; the white mass which then remains is nearly pure dichloroxyepidinic acid. The crude resin, if treated with a sufficient quantity of acetic acid, readily dissolves, forming a solution which soon becomes turbid, and deposits a crystalline powder identical with that which is obtained by repeated washing.

Dichloroxyepidinic acid crystallises with difficulty from alcohol and ether, much more readily from acetic acid. 1 part of it dissolves in 16 parts of boiling acetic acid, and from the cooled solution, the acid after some time separates completely in rhombic laminae. It melts at 182° , gives off 1 mol. H^2O at a higher temperature (about 200°), and solidifies on cooling to a yellowish, transparent, hard, brittle, resinous mass, identical with the resinous product, which yields dichloroxyepidinic acid when treated with potash.

Hydroxyepid, $C^{28}H^{22}O^2$. When 1 part of octohedra¹ oxyepid is boiled with 14 parts of acetic acid and a small quantity of zinc, the oxyepid dissolves, and on pouring the solution, after a few minutes' boiling, into water, a precipitate is obtained, which when washed, dried, and drenched with thirty parts of ether, dissolves partially, leaving a residue of hydroxyepid amounting to about 15 per cent. of the oxyepid employed, while the larger portion which passes into solution consists of lepidin. Hydroxyepid may also be prepared by mixing the solution of 1 part octohedral oxyepid in 42 parts of boiling acetic acid with twice its volume of alcohol, adding small pieces of sodium-amalgam (Na^2Hg) till the liquid on cooling no longer deposits a granular crystalline precipitate, pouring the solution into water, and treating the precipitate with ether as above. The quantity of hydroxyepid thus obtained is about 18 per cent. of the oxyepid employed. Needle-shaped oxyepid heated in acetic acid solution with zinc does not yield any product sparingly soluble in ether, but appears to be entirely reduced to lepidin. On the other hand, by boiling 1 part of needle-shaped oxyepid with 20 parts of alcohol; gradually adding sodium-amalgam and acetic acid in such proportion as to keep the liquid constantly neutral; decanting the solution after some time ($1\frac{1}{2}$ hour per 10 grams of oxyepid, after addition of 150 grams of sodium-amalgam) from the crystalline deposit (which amounts to a third of the weight of the oxyepid employed); and crystallising this deposit from boiling acetic acid—hydroxyepid is obtained, agreeing in its properties with that above described. The alcoholic solution decanted from the crystals contains lepidin.

Hydroxyepid, after purification by washing with a little ether and crystallisation from acetic acid, forms long flat delicate needles, nearly insoluble in cold alcohol and ether. 112 parts of boiling acetic acid dissolve only 1* part of hydroxyepid, and 99 per cent. of that which is dissolved crystallises out on cooling. It melts at 251° .

Hydrodichloroxyepid, $C^{28}H^{20}Cl^2O^2$, is produced by boiling dichloroxyepid—either the needle-shaped or the sparingly soluble modification (p. 1173)*—with zinc and acetic acid, and pouring the resulting solution into water, whereby a curdy precipitate is obtained which is a mixture of dichlorolepidin, m. p. 166° (p. 1173), soluble in ether, and hydrochloroxyepid, which is insoluble in ether, and may be purified by crystallisation from acetic acid or xylene. The yield amounts to about

* Zinin's statements on this point are somewhat contradictory. In 1875 (*N. Petersb. Acad. Bull.* xx. 547) he stated that needle-shaped dichloroxyepid dissolved in acetic acid does not appear to be altered even by prolonged boiling with zinc; but in 1876 (*ibid.* xxi. 66) he says this dichloroxyepid is converted by the same treatment into dichlorolepidin and hydrodichloroxyepid.

25 per cent. of the dichloroxyepidid employed. The same body is obtained by boiling sparingly soluble dichloroxyepidid with 40 parts alcohol, and adding sodium-amalgam and acetic acid by small portions, till the granular deposit is converted into a mass of minute needles: the yield is about 30 per cent. The best mode of preparation however is to boil 20 grams of needle-shaped dichloroxyepidid with 400 grams alcohol, adding sodium-amalgam and acetic acid in such proportions that the liquid may constantly remain acid. After two or three hours—during which time 150–200 grams amalgam will have been added—the liquid, while still hot, is decanted from the deposit; the latter, after washing on a filter, first with alcohol and then with a little water, is boiled with 180 grams acetic acid; and the solution is decanted hot, and again boiled with an equal quantity of acetic acid. The residuo (8–9 grams) is nearly pure hydrodichloroxyepidid.

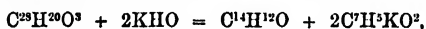
Hydrodichloroxyepidid is quite insoluble in alcohol and in ether, but dissolves in 205 parts boiling acetic acid, and separates therefrom in flat, rather long needles, melting at 261° .

Hydrodibromoxyepidid, $C^{28}H^{20}Br^2O^2$, is prepared, like its chlorine analogue, by the action of zinc and acetic acid on dibromoxyepidid (needle-shaped or sparingly soluble), the product being a mixture of dibromolepidin soluble and hydrodibromoxyepidid insoluble in ether. The latter is but very slightly soluble in alcohol as well as in ether, but dissolves in 172 parts of boiling acetic acid, and crystallises therefrom in needles.

Dioxyepidid, $C^{28}H^{20}O^3$, is known in two modifications, one formed from needle-shaped, the other from octohedral oxyepidid.

(1). Needle-shaped oxyepidid (25 grams) in fine powder is drenched with 20 grams acetic acid, a solution of 12 to 15 grams chromic acid in 150 grams glacial acetic acid is added, and the whole is cautiously heated to 90° – 95° , till the liquid exhibits a yellow but not a blue colour. The resulting solution on cooling deposits the dioxyepidid in large rhombic, nearly square plates, which may be purified by washing with alcohol and recrystallisation from alcohol.

This dioxyepidid melts at 157° , and solidifies to a resin, which again becomes crystalline at 150° . It dissolves in 24 parts of 95 per cent. alcohol at the boiling heat, the cooled solution retaining only $\frac{1}{10}$ th part of it. It is nearly insoluble in cold crystallisable acetic acid, but dissolves in about its own weight of the same acid at the boiling heat. Chromic acid oxidises it to benzoic acid and benzile; reducing agents have no effect upon it. Alcoholic potash, even when dilute, resolves it into dioxybenzoïn and benzoic acid:



whence its rational formula is $C^{14}H^{10}(C^7H^5O)^2O$ (Zinin, *Zeitschr. f. Chem.* vii. 483).

(2). The other modification of dioxyepidid, $C^{28}H^{20}O^3$, is obtained by boiling 1 part octohedral oxyepidid with 6 parts acetic acid, adding crystals of chromic acid by small quantities, the action of each being allowed to complete itself before a further portion is added, and pouring the liquid into water as soon as all the oxyepidid is dissolved, and no more crystals appear to form on cooling. By recrystallising the product from alcohol, dioxyepidid is obtained in white, nacreous, striated, rhombic plates, melting at 164° . The yield amounts to about a third of the oxyepidid used, the remainder being oxidised to benzoic acid. 1 part of this dioxyepidid dissolves in 10 parts boiling alcohol, and 4 parts boiling acetic acid. In ether it is less soluble than in alcohol. It is distinguished from the preceding modification by its melting point, and by its resistance to the action of alcoholic potash, which does not affect it, even when concentrated and at the boiling heat (Zinin, *N. Petersb. Bull.* xx. 547).

Isolepidin, $C^{28}H^{20}O$ (Zinin, *Bull. Soc. Chim.* [2], xxvii. 456; *Deut. Chem. Ges. Ber.* v. 1104; x. 80). This compound, isomeric with lepidin, is produced by the dry distillation of either of the three oxyepidids above mentioned, and may be purified by washing the distillate with a small quantity of ether, treating it with alcoholic potash, and recrystallising from alcohol. It dissolves in 18 parts of boiling and 266 parts cold alcohol of 95 per cent., and crystallises in four-sided plates, which do not lose weight at 130° and melt at 150° . It dissolves also in 2 pts. of boiling acetic acid. By distillation it is partly decomposed and converted into a resinous mass. Alcoholic potash does not affect it. By oxidising agents it is converted first into oxyisolepidin, and finally into benzophenone, with benzoic acid and a small quantity of benzile as secondary products.

Dihydro-isolepidin, $C^{28}H^{20}O$, is formed by the action of zinc-dust on a solution of isolepidin in 5 or 6 pts. of glacial acetic acid, and may be separated by pouring the green liquid portion of the product into water, whereby a precipitate is formed, which is to be washed, dried, and treated with ether (to remove a resinous colouring

natter), and finally purified by crystallisation from boiling alcohol. It is thus obtained in small rectangular prisms which melt at 182° , dissolve very slightly in ether, in 12½ pts. boiling acetic acid, and 95 parts alcohol of 95 per cent. It is very slowly attacked by chromic acid and other oxidisers; more easily by phosphorus pentachloride than isolepidin.

Tetrahydro-isolepidin, $C^{28}H^{24}O$, is produced by the action of sodium-amalgam on a boiling alcoholic solution of isolepidin (15 to 20 pts. Na^2Hg to 1 pt. isolepidin), or more advantageously on dihydro-isolepidin, and is separated from the crude product by distilling off the greater part of the alcohol, and pouring the residue immediately into water, whereby a precipitate is obtained, soft and resinous at first, but hardening after washing and prolonged boiling with water. On dissolving this mass in ether, and leaving the ether to evaporate, the tetrahydro-isolepidin separates, at first as a soft resinous mass, which afterwards coagulates in crystalline lumps. These melt at 132° , and resolidify to a translucent resin; they dissolve readily in acetic acid and in alcohol, somewhat less easily in ether. By chromic acid in acetic acid solution, tetrahydro-isolepidin is reconverted, even at ordinary temperatures, into dihydro-isolepidin.

Oxyisolepidin or Isoxylepidin, $C^{28}H^{20}O^2$. This compound, as already observed, is the first product of the action of oxidising agents on isolepidin. To prepare it, a solution of 3 pts. isolepidin in 40 pts. acetic acid is mixed with a solution of 3 pts. chromic acid in 30 pts. acetic acid, and the tufts of needles which separate in the course of 24 hours are separated from the supernatant liquid and purified by crystallisation from boiling alcohol. In preparing this compound, it is not advisable to operate on more than 5 grams of isolepidin at a time, as when larger quantities are used, a rise of temperature takes place, which leads to the formation of a large quantity of benzile as a bye-product.

Oxyisolepidin thus prepared crystallises in short, thin, dull-white needles, melts at 160° , dissolves in 40 pts. boiling and 600 pts. cold alcohol, in 4 pts. boiling acetic acid, freely also in boiling benzene, from which it crystallises in nodular groups of quadrangular plates. It is not altered by boiling alcoholic potash. It appears to be dimorphous, for when an ethereal or alcoholic solution of the compound, which no longer yields needles on cooling, is left to evaporate, it deposits wedge-shaped crystals with quadrangular base, having the same composition as the needles. The same crystals may be obtained directly by boiling the ordinary needle-shaped crystals for some time with a quantity of alcohol not sufficient to dissolve them completely, or more easily from a solution of the needles in alcoholic potash. The wedge-shaped oxyisolepidin melts at 162° , and when heated above its melting point till a rapid evolution of gas-bubbles takes place, assumes an orange-brown colour, and solidifies on cooling to a translucent resin, from which ether (10–15 pts. to 1 pt. of the resin) extracts a crystalline body; and this latter, when purified by washing with ether, and recrystallised from alcohol or glacial acetic acid, forms rhombic plates very slightly soluble in ether, dissolving in 13.5 pts. boiling acetic acid and 80 pts. boiling alcohol, and melting at 152° . This substance, which may also be obtained by distilling the oxyisolepidin above described, and exhausting the distillate with ether, appears from its composition and properties to be an isomeric oxyisolepidin.

Oxyisolepidin dissolved in acetic acid and treated with zinc is converted into the above-described dihydro-isolepidin. When oxidised by chromic acid (2 pts. to 1 pt. oxyisolepidin) in acetic acid solution at the boiling heat, it yields four bodies—namely, an oily substance in very small quantity, benzoic acid, benzile, and as chief product, benzophenone. The oily substance may be removed, by subjecting the half-solidified mass to pressure, and the benzophenone may be separated by boiling the residue with a weak solution of potash in alcohol of 40 per cent., and precipitating with water.

Oxylepidinic acid, $C^{28}H^{22}O^3$, is formed as a secondary product in the preparation of isolepidin, and is found in the alcoholic potassic mother-liquor which remains after the purification of that substance (p. 1176); it may be obtained in larger quantity by exhausting the crude distillation product of the oxylepidins with ether, and boiling the resin which remains on evaporating the ether with alcoholic potash. The acid thereby dissolved may be separated by pouring the solution into water, heating the liquid to expel the alcohol, and precipitating with acetic acid; and purified by dissolving the crude product in aqueous potassium carbonate, precipitating fractionally with acetic acid, repeating these operations if necessary, and recrystallising the last precipitated portions from acetic acid. Oxylepidinic acid dissolves in 2 pts. of boiling acetic acid, and melts at 168° (Zinin).

LEPIDINE, $C^{30}H^{20}N$. When sodium-amalgam is added to lepidine, the mixture becomes hot, acquires a reddish-brown colour, and finally solidifies. Water added to

this product separates a yellowish oil, which, when boiled with water and an acid, yields a deep reddish-brown solution, depositing as it cools crystals of a splendid scarlet colour. These crystals must be dried in the dark, since they are altered in colour by light, as is also the case with silk or wool dyed with this substance. When nitric acid was used, the solution on cooling gave a crop of red crystals having the composition of *dilepidine nitrate*, $C^{20}H^{18}N^2.HNO^3$. Chinoline behaves in a similar manner, the red substance yielding with hydrochloric acid, crystals of *dichinolite hydrochloride*, $C^{14}H^{14}N^2.HCl$ (C. Greville Williams, *Chem. News*, xxxvii. 85).

LEPIDIUM. The volatile oil of garden cress (*L. sativum*) has been shown by Hofmann to consist of α -toluonitril, $C^8H^5.CH^2.ON$ (see *CHASS OILS*, viii. 584).

LEPIDOLITE. On the preparation of Lithium from this mineral, see *LITHIUM*.

LESLEYITE. This name has been applied to certain micaceous minerals, accompanying corundum in Chester Co., Pennsylvania, and in North Carolina, which have been regarded by some mineralogists as forming a distinct species, but according to Brush and Genth, are mixtures of corundum with damourite and diasporite, or with damourite alone (see *Jahresb. f. Chem.* 1869, 1219; 1873, 1153).

LETTSSOMITE. This mineral, originally found, in small quantities, in the Bannat, has lately been obtained from the Garonne mine, Département du Var, where it occurs in radiate groups of capillary crystals forming thin coatings on slabs of sandstone. The following analysis by Pisani (*Compt. rend.* lxxvi. 1418) agrees closely with that by Percy of lettssomite from the Bannat:

SO ³	CuO	CaO	Al ² O ³	Fe ² O ³	H ² O
12.10	49.00	2.97	11.21	1.41	22.50 = 99.19

Pisani considers lettssomite as a distinct species, both on account of its fibrous structure, and of the close resemblance in composition shown by specimens collected from two localities so widely separated as those above mentioned.

LEUCANILINE. $C^{20}H^{21}N^2$ (iii. 574; vii. 733). A base supposed to be identical with leucaniline is formed, with evolution of ammonia, by heating rosaniline or its acetate to about 192° with excess of dimethylaniline. The product freed from dimethylaniline by distillation and treatment with steam, is a brownish resinous mass, from the solution of which in hydrochloric acid, the greater part of the impurities present may be thrown down by addition of common salt. By separating the base with an alkali, and repeating this treatment several times, it is obtained pure, and then melts at 86° (Nietzki, *Arch. Pharm.* [3], v. 41). According to Hofmann, leucaniline melts at 100°. Dale a. Schorlemmer (*Deut. Chem. Ges. Ber.* x. 1016, 1123) obtain leucaniline by heating aurin with alcoholic ammonia at 150° for several days, or with aqueous ammonia to 120° for twenty hours. E. and O. Fischer (*Ber.* xi. 1079), by oxidising a solution of trinitrophenylmethane in glacial acetic acid with chromic acid, obtained a white crystalline trinitrocarbinol, $C^{10}H^{12}(NO^2)^3OH$, melting at 171°–172°, which, when treated with zinc dust, yielded paranitrorosaniline and finally leucaniline.

Diazo-leucaniline Chloride, $C^{20}H^{18}N^2Cl^2$, prepared in the ordinary way, is a light yellow glutinous mass, which unites with auric chloride, forming the double salt $C^{20}H^{18}N^2Cl^2 + 3AuCl^3$. The chloride dissolves in water, forming a greenish-blue solution, which decomposes when boiled, depositing a dingy brown precipitate only partially soluble in potash.

The hydrocarbon, $C^{20}H^{18}$, corresponding with this diazo-compound, is not easily prepared from the latter when once it has been separated and thereby rendered sparingly soluble in alcohol; but it may be obtained by the following method: 300 grams of leucaniline are dissolved in 1500 g. strong sulphuric acid; the solution, in portions of 40 g. each, is treated with nitrous acid, and after the excess of the latter has been expelled by a strong current of air, each of these portions is slowly added to 250 g. boiling alcohol. The several portions of liquid are then united; the whole is neutralised with sulphuric acid; evaporated to one-fourth of its bulk; then largely diluted with water; and the oil thereby separated is extracted with ether. After the evaporation of the ether, there remains a dark brown oily residue which may be freed by soda-ley from sulphoacids and phenolic bodies. On again exhausting with ether and distilling, the greater part of the liquid (85 g.) passes over above the range of the mercurial thermometer, while a small carbonaceous residue remains in the retort. The liquid thus obtained, having been completely dehydrated with sodium and again rectified, yields 55 g. of a light yellow heavy oil which has a faint bluish fluorescence, and thickens in a freezing mixture without solidifying, but separates in the crystalline state after a few days from a hot saturated solution in methyl alcohol; the concentrated mother-liquors solidify partially after several months. By repeatedly crystallising this product from methyl alcohol, the hydrocarbon, $C^{20}H^{18}$, is obtained in spherical groups of colourless

prisms, melting at 58° , and boiling without decomposition at a temperature above 360° . It dissolves easily in ether, benzene, and ligroin, sparingly in cold alcohol, and shows but little tendency to crystallise. Treated in acetic acid solution with fuming nitric acid, and with bromine, it yields solid nitro- and bromo-derivatives which crystallise with difficulty. By oxidation with chromic acid it is converted into a ketone, $C^{10}H^{16}O$, which crystallises from hot ligroin in nodular groups of colourless laminae, softens at 143° , melts at 148° – 149° , and appears to be completely decomposed by further oxidation (E. and O. Fischer, *Ber.* ix. 891).

LEUCAURIN, $C^{20}H^{16}O^3$. See vol. vii. p. 119.

LEUCIN. See PROTEIDS.

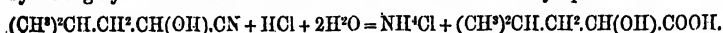
LEUCHTENBERGITE. This mineral, from Slatoust in the Ural, regarded by some mineralogists as a distinct species, by others as a variety of pennine or clinocllore (i. 914; iii. 575; vi. 782), has been further examined by Duke Nicholas von Leuchtenberg (*N. Petersb. Acad. Bull.* ix. 188; xxi. 509). The specimen analysed, and regarded as normal, was obtained from the Chichime mountains. It forms large hexagonal plates, easily split at right angles to the optic axis. The laminae thereby separated are translucent, with a fatty to nacreous lustre, white or faint greenish colour, and difficultly friable like talc; in polarised light they exhibit the appearance of uniaxial crystals. Hardness 2.5. Sp. gr. 2.61–2.64. Analysis gave the following composition, agreeing with Descloizeaux' formula for clinocllore, $6SiO_2 \cdot 2Al_2O_3 \cdot 9MgO + 7H_2O$:

SiO_2	Fe_2O_3	CaO	MgO	Al_2O_3	H_2O	
30.46	2.22	0.11	34.52	19.74	12.74	99.79

Leuchtenbergite must accordingly be regarded as a distinct mineral species belonging to the chlorite family.

Microscopical examination of fresh and decomposed material showed the following enclosed minerals: garnets, cubic and prismatic forms, which were regarded as perovskite, and lastly needles, the species of which could not be determined. By weathering, the colour of the mineral is changed to yellowish and afterwards to dark green; the facility of cleavage is diminished; and in certain stages of the alteration, the mass appears interspersed with granules, some of which exhibit the optical characters of quartz.

LEUCIC ACID, $C^6H^{12}O^3$, and **LEUCINITRIL**, $C^6H^{11}NO$. Erlenmeyer a. Sigel (*Deut. Chem. Ges. Ber.* vii. 1109), by combining hydrogen cyanide with valeraldehyde, $C^5H^{10}O$, from fermentation amyl-alcohol, have obtained the true leucinitril, $(CH_3)^2CH.CH^2.CH(OH).CN$, differing essentially from the body to which that name has hitherto been attached (vi. 782; vii. 734), inasmuch as it is completely resolved by fuming hydrochloric acid into sul-ammoniac and leucic or oxycaproic acid:



Leucinitril is a colourless oil of agreeable odour, lighter than water, not quite insoluble therein, soluble in all proportions of ether and alcohol. It does not alter at 100° , but is resolved at higher temperatures into valeraldehyde and hydrogen cyanide.

Leucic acid, obtained as above, may be separated from the sul-ammoniac solution by ether, and remains, on evaporating the ether, as a syrup which gradually solidifies to large transparent crystalline laminae. It is very soluble in water, alcohol, and ether.

N. Ley (*Ber.* x. 231) has also prepared from valeraldehyde, by means of hydrocyanic and hydrochloric acids, an acid which agrees in most respects with leucic acid, but melts at 54° – 55° , whereas leucic acid, according to Wüge (iii. 576), melts at 73° . Ley's acid is oxidised by chromic acid mixture to carbon dioxide, an acid having the composition $C^6H^{10}O^3$, and valeral.

Putrefaction of Leucic Acid.—A mixture of 10 grams calcium leucate, 10 calcium carbonate and 50 putrid fibrin in 12 litres of water was found to yield, as gaseous products, CO_2 , CH_4 , and H , and as liquid products, caproic, butyric, and acetic acids (J. Stolnikoff, *Zeitschr. physiol. Chem.* i. 345).

LEUCINE or **AMIDOCAPROIC ACID**, $C^6H^{11}NO^2 = C^6H^{10}(NH^2)^2.CO^2H$.

Occurrence in Plants.—The juice of vetches grown in moist garden-soil and germinated in the dark—perfectly fresh and freed from albuminoids by boiling and partly also by dialysis—has been found to contain, together with asparagine, a not inconsiderable quantity of leucine, both these bodies being doubtless produced by transformation of proteids stored up in the seed. When the mother-liquor decanted from the asparagine was somewhat further concentrated, crystalline crusts separated, after a short time, on its surface, appearing under the microscope as groups of well-defined spherules, and exhibiting all the reactions of leucine (Gorup-Besanez, *Berl. Ber.* vii. 146; see

also Cossa, *Gazz. chim. ital.* 1875, 314). The basic substance called *chenopodine*, which Reinsch obtained from *Chenopodium album* (vii. 429), is regarded by Gorup-Besanez as identical with leucine.

Leucine has also been found in small quantities, together with tyrosine and glutamic acid, in young pumpkin-plants (Schulze a. Barbieri, *Ber.* xi. 1233).

On the occurrence of leucine in the aqueous extract of yeast, see FERMENTS (p. 783).

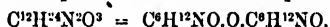
Formation.—*a.* Together with tyrosine, asparagine, glutamic acid, and ammonia, by the action of stannous chloride on albumin animal or vegetable, casein, and legumin dissolved in hydrochloric acid (Hlasiwetz a. Habermann), see PROTEIDS. *β.* Together with ammonia, glycocine, tyrosine, a yellowish body called *gelatin peptone*, and a very small quantity of indole, by the pancreatic digestion of gelatin (Nencki, *Ber.* vii. 1593). Jeanneret (*J. pr. Chem.* [2], xv. 353), by subjecting gelatin for eleven days to the action of the organised ferments of the pancreas, in a vessel from which the air was excluded, obtained leucine, but when the air had access to the vessel, no formation of leucine was observed.

Density.—According to Engel a. Vilmain (*Bull. Soc. Chim.* [2], xxiv. 279), the specific gravity of leucine is 1.293 at 18°.

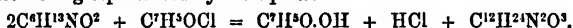
Oxidation.—Leucine is converted by oxidation into carbamic acid, which indeed appears to be invariably produced by the oxidation of nitrogenous carbon-compounds in alkaline solution, or generally when carbon dioxide and ammonia come together in the nascent state (Drechsel, *J. pr. Chem.* [2], xii. 417). See also CARBAMIC ACID (p. 382).

Reaction with Urea.—When leucine and urea are fused together, a compound is formed which crystallises in needles and appears to consist of uramido-caproic acid (Huppert a. Hofmeister, *Ber.* vi. 1278).

Reaction with Benzoyl Chloride.—When thoroughly dried leucine is heated to 100° with benzoyl chloride, the mixture fuses and turns yellow, while benzoic acid separates on the surface in long needles, the reaction being terminated as soon as the evolution of hydrochloric acid ceases. On treating the mass with tepid water to remove the benzoic acid, a yellow substance is left partly soluble in hot alcohol, and the portion insoluble in that liquid consists of amidocaproic anhydride,



its formation being represented by the equation



Amidocaproic anhydride is a white amorphous body, which becomes gelatinous when repeatedly washed with boiling alcohol, and is not easily reconverted into leucine even by prolonged boiling with water. The portion soluble in alcohol consists of *dibenzoyl-amidocaproic anhydride*, $(\text{C}^6\text{H}^{12}\text{NO.O.C}^6\text{H}^5\text{O})^2\text{O}$. It is yellow and amorphous, soluble in alcohol, insoluble in water, melts at 85°, is resolved by boiling with water into benzoic acid and amidocaproic anhydride, and decomposes when heated on platinum foil, giving off benzoic acid (A. Destrom, *Compt. rend.* lxxxvi. 484).

LEUCINITRIL, see p. 1178.

LEUCITE. This mineral, hitherto known only as of European occurrence, has been found by Vogelsang—together with augite, plagioclase, sanidin, and small quantities of magnesia-mica and apatite—as a constituent of the basalt of Gunung Bantal Soesoem, on the small island of Bawean, near the north coast of Java (F. Zinkel, *Min. Mitth.* 1875, 227). According to F. A. Anger (*Min. Mitth.* 1875, 153) leucite is the chief constituent of the trass of Lake Laach and of the Ries.

Crystalline Form.—Vom Rath inferred, from the measurement of the angles of leucite, and from the striation of its faces, which indicates twin-formation, that it belongs, not to the regular system, as generally supposed, but to the quadratic system (vii. 767). Scacchi, on the other hand (*Zeitschr. geol. Ges.* xxiv. 503), regards the mineral as belonging to the regular system, and attributes the difference in the angular measurement to errors of observation. Hirschwald also (*Min. Mitth.* 1875, 227) regards leucite 'as a regular crystal-species with polysymmetric development in the direction of the quadratic system.' Vom Rath (*Pogg. Ann. Ergänzbd.* vi. 198) defends his conclusions respecting the quadratic form of leucite, and controverts the difference supposed by Scacchi to exist between implanted and imbedded leucite. He also demonstrates the quadratic form of the sublimed leucites occurring, as first observed by Scacchi, in small cavities, and formed by the disintegration of old leucites. The analysis of these sublimed crystals gave

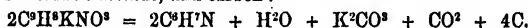
56.5 per cent. SiO_2 , 25.3 Al_2O_3 , 16.2 K_2O , and 2.8 Na_2O .

H. Baumbauer (*Zeitschr. Kryst.* i. 257) confirms the views of vom Rath, particularly

with regard to the twin-formation of leucite. That the ordinary form of leucite is not a simple form, but a combination, is shown by the behaviour of the crystals to etching liquids, by which the ditetragonal pyramid-faces are more strongly attacked than the tetragonal faces. The optical characters of leucite also show that its form is not monometric. Tschermak (*Berl. Acad. Ber.* 1876, 695) examined a leucite free from twin-lamination, found in the lava of Acquacetosa near Rome, and found it to be negatively double-refracting. This leucite, analysed by Berwerth, gave 55.18 per cent. SiO_2 , 23.65 Al_2O_3 , 0.83 CaO , 19.40 K_2O , and 0.32 Na_2O (=99.38), with traces of iron and magnesium.

LEUCOGALLOL, $\text{C}^5\text{H}^{10}\text{Cl}^{10}\text{O}^{12}$, or $\text{C}^5\text{H}^{10}\text{Cl}^{12}\text{O}^{14}$. A compound formed by the action of chlorine at low temperatures on pyrogallol in presence of acetic acid (see, PYROGALLOL).

LEVULINIC ACID, $\text{C}^5\text{H}^8\text{NO}^3$ (J. Dewar, *Proc. Roy. Soc.* xxvi. 65). This acid is formed by oxidising leucoline sulphate (43 parts dissolved in 200 water) with potassium permanganate (100 in 1000 water). It crystallises in colourless lamellæ or needles melting at 162° ; is somewhat volatile in a stream of hydrogen at 110° , also in a stream of aqueous vapour, to which it imparts a peculiar aromatic odour; is slightly soluble in cold, more soluble in warm water; crystallises from alcohol and ether with a faint coloration due to slight oxidation. Its salts, excepting the plumbic, ferric, and mercurous salts, are easily soluble; the silver salt forms slender needle-shaped crystals. The acid heated above its melting point suffers partial decomposition, and yields a sublimate, probably consisting of the anhydride. Heated to low redness with soda-lime, it yields aniline, together with ammonia and a small quantity of picoline; when potash-lime is used, the aniline obtained is almost free from picoline. *Potassium leucanilate*, heated by itself yields aniline, water, potassium carbonate, free carbon dioxide, and carbon:



By fusion with excess of potash, the acid is resolved into carbon dioxide, ammonia, hydrogen, and salicylic acid, the last being probably formed from anthranilic acid produced in the first instance:

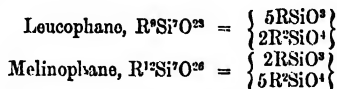


The acid, heated with glycerin to the boiling point of the latter, likewise yields aniline, together with small quantities of a substance having the properties of indole.

LEUCOPHANE and **MELINOPHANE**. Rammelsberg (*Berl. Acad. Ber.* 1876, 23) has analysed leucophane (Nos. 1-4) and melinophane (Nos. 6-10), and refers them to the following formulæ:



If we suppose $2\text{Na} = \text{R}''$, $\text{F}^2 = \text{O}$, and therefore $6\text{NaF} = 3\text{R}''\text{O}$, we shall have for these minerals the formulæ,



the analogy of which is perhaps more than accidental.

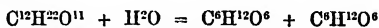
	F	SiO^2	BeO	CaO	Na_2O	K_2O
1 (found)	6.57	47.03	11.73	23.61	11.26	0.30
2 "	6.53	undet.	12.25	23.52	10.27	0.30
3 "	6.97	47.07	11.25	22.92	undetermined	
4 "	6.91	49.70	12.40	23.68	undetermined	
5 (calc.)	6.69	49.35	11.16	24.68	10.93	—
6 (found)	5.73	43.66	13.31	26.82	8.55	1.40
7 "	5.43	41.40	13.81	29.05	undetermined	
8 "	6.39	44.32	13.84	29.93	undetermined	
9 "	undetermined		14.04	30.10	7.21	0.59
10 "	undet.	42.50	13.62	30.56	undet.	undet.
11 (calc.)	5.83	42.95	13.60	30.07	8.56	1.44

LEUCOROSOLIC ACID. See ROSOLIC ACID.

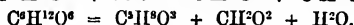
LEVULINIC ACID, $\text{C}^5\text{H}^8\text{O}^3$ (Grote a. Tollens, *Deut. Chem. Ges. Ber.* vi. 1390; vii. 1375; x. 1440; *Liebig's Annalen*, clxxv. 181; F. Bonte, *Ber.* viii. 416). This

acid is formed by boiling cane-sugar with sulphuric acid, the cane-sugar being first resolved into dextrose and levulose, the latter of which appears to be the chief source of the levulinic acid, inasmuch as when the acid produced as above described is neutralised with chalk and the resulting calcium salt is crystallised out, a mother-liquor is obtained containing dextrose, whereas the levulose disappears entirely. A small quantity of levulinic acid is however obtained by treating dextrose alone with sulphuric acid.

The method originally given by Grote & Tollens for the preparation of levulinic acid was somewhat complex, but in their latest communication (*Ber.* x. 1440) the following simpler method is described. A mixture of 1000 grams of sugar-candy, 1000 grams of water, and 1000 grams of ordinary sulphuric acid, is heated in a salt bath for four days; the resulting liquid is agitated ten or twelve times with ether; the ether is distilled off, and the residue is heated on the water-bath, and afterwards distilled. Formic acid then passes over first, and afterwards between 218° and 225° levulinic acid, which solidifies after repeated distillation, its boiling point then rising to 235°-255°. The formation of levulinic and formic acids from cane-sugar is represented by the equation—



and



Filter paper and deal shavings boiled with sulphuric acid also yield levulinic acid, but in small quantity only; Curagheen moss yields about as much as cane-sugar (Bente).

Pure levulinic acid melts at 33.5°. It is optically inactive, dissolves in water in all proportions, is not perceptibly acted upon by bromine. Heated for three days in a salt bath with 20 times its weight of 5 per cent. sulphuric acid it turns yellow, but deposits only a few flocks.

Calcium levulinate, $(C^3H^5O^3)_2Ca.2H^2O$, obtained by neutralising the acid with calcium carbonate, crystallises in silky needles often a centimeter long, dissolves very freely in water, and forms syrupy solutions which deposit crystals but slowly. It melts at 100°, giving off the greater part of its water of crystallisation, the rest of which is expelled at 130°-140°. A salt with 1 mol. H^2O was likewise obtained, but Grote & Tollens are not sure that it was pure. The *zinc salt*, $(C^3H^5O^3)_2Zn$, also prepared by neutralisation, crystallises in silvery needles or laminae, the latter of which appear under the microscope to be made up of needles. It dissolves easily in water and in alcohol, especially when warm, is slightly soluble in absolute alcohol, and forms syrupy solutions. The *silver salt*, $C^3H^5O^3Ag$, formed by precipitation, crystallises from a boiling solution in well-defined, elongated, six-sided plates, whose two acuter angles measure on the average 99° 6', and the four obtuser angles 131° 30'. It dissolves at 17° in about 150 parts of water. The *potassium salt*, prepared from the silver salt by double decomposition with potassium carbonate, solidifies over sulphuric acid to nodular groups of microscopic needles. The *ammonium salt* forms small needles; the *barium salt* was obtained only in the form of an uncrystallisable gummy mass.

Grote & Tollens have also examined the so-called glucates, which Mulder prepared by the action of lime or baryta on glucose (ii. 488), and concludes that his acid calcium glucate is identical with the levulinate. His neutral glucates they regard as formed by the action of the lime or baryta on sugar contained in the mother-liquor of the crystallised calcium levulinate.

For the constitution of levulinic acid, Grote & Tollens regard two views as possible: either that this acid contains a hydroxyl-group, in which case it may be represented by a ring-formula similar to that proposed by Limpricht for pyromucic acid (vi. 979); or (2) that one of its oxygen-atoms may be situated as in acetone or in ethylene oxide, in which case it must be regarded as a homologue of pyracemic acid, $CH^3.CO.CO.OH$. This latter view of its constitution is adopted by Conrad (*Liebig's Annalen*, clxxxviii. 223), who regards it as identical with β -acetopropionic acid, $CH^3.CO.CH^2.CO.OH$, formed by the action of baryta-water on ethylic acetosuccinate (see PROPIONIC ACID). The close resemblance of these two acids in nearly all their properties has been further demonstrated by the recent experiments of Grote & Tollens (*Ber.* x. 1440), thus:

Levulinic acid	β -Acetopropionic acid
m. p. 32.5-33.5	31°
b. p. 235°-255°	239°
Ethylic Ethers	
b. p. 200°-201°	203°-205°

The silver salts of both acids are slightly soluble; their other salts easily soluble. The only point of difference observed is in the calcium salts, the levulinate crystallising with 2 mol. water, whereas the β -acetopropionate is anhydrous.

LEVULOSE. See SUGARS.

LIBANITE. See RESINS, FOSSIL.

LICHENIN, $C^6H^{10}O^5$. This carbohydrate, and a substance turned blue by iodine, existing together with it in *Cetraria islandica* (iii. 586), have been further examined by Th. Berg (*Russ. Zeitsch. Pharm.* 1873, 129, 161). The lichen is repeatedly boiled with fresh portions of water till the extract is no longer rendered turbid by alcohol. The strained extracts when left at rest for twenty-four hours, deposit the lichenin as a jelly, which is freed from a bitter principle and the substance which gives the blue colour with iodine, by filtration through linen, and washed with water till the blue reaction with iodine is no longer visible. The jelly remaining on the filter is then dissolved in hydrochloric acid, precipitated with alcohol, pressed, and slowly dried; the filtrate is concentrated to a small bulk and precipitated with alcohol; and the precipitate of the substance turned blue by iodine, which soon becomes glutinous, is thoroughly washed with alcohol and then dried. Both the lichenin and the substance turned blue by iodine have the composition $C^6H^{10}O^5$. Lichenin does not yield sugar either when boiled with water or when treated with malt-extract, saliva, pancreas extract, or gastric juice, but it is converted into sugar by boiling with sulphuric or hydrochloric acid. The substance turned blue by iodine yields a little sugar when boiled for a long time with water, and is easily and completely converted into sugar by treatment with an acid. Lichenin, immersed in glacial acetic acid, swells up without dissolving, and on heating the liquid to 100° , a jelly is formed, having the composition $C^6H^{10}(C^2H^3O)^3O^5$. The substance turned blue by iodine is not altered by glacial acetic acid. Neither this latter substance nor lichenin is turned blue by treatment with sulphuric acid and iodine together; both dissolve in zinc chloride; Schweizer's reagent dissolves only the lichenin. Alcoholic potash at the boiling heat acts somewhat strongly on lichenin, very slightly on the substance turned blue by iodine. Lichenin forms compounds with potash and soda; the substance turned blue by iodine does not. No method has yet been found of converting either of these substances into the other.

LICHNOXANTHIN. See PLANTS, COLOURING MATTERS OF.

LIEVRITE. Analyses of this mineral from Elba by Stüdeler (*J. pr. Chem.* xcix. 70), and by Sipöcz (*Liebig's Annalen*, clxxviii. 196), lead to the conclusion that the water, formerly regarded as accidental (iii. 589), is an essential constituent, and that the mineral may be represented by the formula $6RO.Fe^2O^3.4SiO^2.H^2O$, in which $R = \frac{2}{3}Fe + \frac{1}{3}Ca$. Analysis (1) by Stüdeler, of black, shining, crystalline masses; sp. gr. 4.023; (2) by Sipöcz, mean of four, made on carefully selected material; sp. gr. 4.037:

SiO^2	Fe^2O^3	FeO	MnO	CaO	H^2O
29.20	20.74	35.15	—	12.90	2.36 = 100.35
29.67	21.26	33.09	0.74	13.33	2.32 = 100.41

Rammelsberg, on the other hand (*Zeitschr. geol. Ges.* xxii. 897), regards the water (1.65 per cent. according to nine experiments) as the result of weathering, and represents the anhydrous mineral by the formula $R^{12}Fe^2Si^4O^{38}$ or $12RO.2Fe^2O^3.9SiO^2$, in which $R = \frac{2}{3}Fe + \frac{1}{3}(Ca, Mn)$.

An analysis by W. Early of lievrite from Elba, in which especial attention was given to the determination of the two oxides of iron, is published by J. Emerson Reynolds (*Phil. Mag.* [5], iii. 287):

SiO^2	Al^2O^3	Fe^2O^3	FeO	MnO	CaO	MgO	K^2O	Na^2O	H^2O
29.93	0.36	20.16	31.83	3.02	13.71	0.30	0.20	0.29	0.42 = 100.22

Regarding the water as unessential, Reynolds represents the analytical numbers by the formula $6RO.R^2O^3.4SiO^2$, in which $6RO = 4(Fe, Mn)O + 2CaO$.

On the relations of form and composition of Lievrite and Humite, see Websky (*Berl. Acad. Ber.* 1876, 201; *Jahrb. f. Min.* 1876, 660; *Jahresb. f. Chem.* 1876, 1252; *Chem. Soc. Jour.* xxxii. 117).

LIGHT. 1. REFRACTION AND DISPERSION.

A. Of Gases. Mascart (*Compt. rend.* lxxviii. 617; *Pogg. Ann.* cliii. 149) has worked out the following relations between the refractive power and density of gases, in which, instead of the refractive index n , the excess of refraction $n - 1$ is taken into account. This function, if the laws of Boyle and Gay-Lussac were strictly true, should be proportional to the pressure p . Instead of this, Mascart finds from his experiments that

$$n - 1 = a(1 + bp),$$

where a and b are constants. According to Regnault's tables, the density of a gas is very nearly represented by the formula

$$\frac{d}{p} = a'(1 + b'p),$$

so that, if the index of refraction were directly proportional to the pressure, δ would be equal to δ' , which, however, as shown by the following table, is true only as a very rough approximation. Between constant pressures, but at varying temperatures, t , the excess of refraction, $n-1$, should be inversely proportional to the factor $1+\alpha t$, instead of which a variable factor β was found for the several gases. The last column of the table shows the absolute values of 1000 times the excess of refraction ($n-1$) for the sodium-line at the temperature 0° and pressure 700 mm.:

Gases	Compressibility		Refraction		Influence of Temperature	1000(n_0-1)
	t	δ	t	δ	β	
Hydrogen	10°	-0.00057	22°	-0.00087	0.00381	0.1388
Air	5	+0.00107	22	+0.00072	0.00383	0.2923
Nitrogen	5	0.00068	21	0.00085	0.00382	0.2972
" Monoxide . .	9.3	0.00754	13.5	0.0088	0.00388	0.5084
" Dioxide . .	—	0.00225	12	0.00070	0.00367	0.2967
Carbon Monoxide .	—	0.00435	—	0.00089	0.00367	0.3336
" Dioxide . .	3	0.00901	17	0.0072	0.00106	0.4494
Sulphur " . . .	7.7	0.0322	13	0.025	0.00471	0.6820
Cyanogen	—	0.0322	25	0.027	—	0.8202

By the same method Mascart has determined the dispersion of several gases. From Cauchy's dispersion formula, according to which the index of refraction is

$$n = A \left(1 + \frac{B}{\lambda^2} \right),$$

λ being the wave-length, the constant B was found to have the following values:

for Atmospheric Air	0.0058
Nitrogen	0.0069
Hydrogen	0.0044
Nitrogen Monoxide	0.0127
Carbon "	0.0075
" Dioxide	0.0052
Cyanogen	0.0100

Nitrogen monoxide and cyanogen disperse more strongly than water; the dispersive power of atmospheric air is about $\frac{2}{3}$ of that of water, and its value above given agrees almost exactly with that previously found by Ketteler (*Ueber die Farbenstreuung der Gase*, Bonn, 1865).

The following formula for calculating the refractive indices of atmospheric air at different temperatures has been deduced by V. v. Lang (*Pogg. Ann.* cliii. 448) from very careful experiments:

$$n = n_0 - 0.00000905 t + 0.0000000235 t^2,$$

n_0 having, according to the observations of Biot and Arago, the value 1.0002945. These coefficients differ considerably from those of Mascart.

B. Of Liquids.—The influence of Compression on the Refractive Power of Water has been studied by Mascart (*Compt. rend.* lxxviii. 801; *Pogg. Ann.* cliii. 154). Assuming Grassi's coefficient of the compression of water to be correct, it follows from Mascart's experiments that the old law,—deduced from the emission-theory of light—affirming that the specific refractive power of bodies, $\frac{n^2-1}{d}$, is constant for all varia-

tions of density, is utterly wrong, and that the magnitude $\frac{n-1}{d}$, to which the name specific refractive energy is given by Dale a. Gladstone (iii. 625) approximates to a constant value, but not closely enough to be made the foundation of a law.

The method of observation adopted rendered it possible to measure by optical means the fall of temperature produced by sudden decrease of pressure. On the basis of Dale a. Gladstone's values for the decrease of the refractive index of water with rise of temperature (iii. 616), the rise consequent on an increase of pressure of 1 at. was found to be equal to 0.00110, a value agreeing almost exactly with that deduced from the mechanical theory of heat.

Compound Ethers.—The refractive indices of isomeric compound ethers (from fermentation alcohols) have been determined by Pierre a. Puchot (*Compt. rend.* lxxvi. 1566). The ethers of each pair were compared together at the same temperature, a , of the surrounding medium, and the data thus obtained afforded the means of calculating the refractive index which the second ether in the pair would exhibit at a distance from its boiling point equal to that at which the determination was made for the first. As the differences of boiling point Δ never exceeded 1° , the alteration of the boiling point could, for this calculation, be regarded as proportional to the alteration of density. Four comparisons at temperatures a from 15° – 16° yielded the following results, in which t denotes the temperature of the liquid, d_0 its density at 0° , d_t that at the boiling point, l_a the refractive index at the temperature a , and $l_{a-\Delta}$ that at the temperature $a - \Delta$.

	t	d_0	d_t	l_a	$l_{a-\Delta}$
Propyl Butyrate . . .	135.0	0.887	0.745	1.3972	1.3972
Butyl Propionate . . .	135.7	0.893	0.743	1.3981	1.3989
Ethyl Valerate . . .	135.5	0.886	0.744	1.3981	1.3981
Butyl Propionate . . .	135.7	0.893	0.743	1.3981	1.3983
Propyl Butyrate . . .	135.0	0.887	0.745	1.3972	1.3972
Ethyl Valerate . . .	135.5	0.886	0.744	1.3981	1.3973
Butyl Acetate . . .	116.5	0.905	0.778	1.3901	1.3901
Methyl Valerate . . .	117.5	0.901	0.774	1.3937	1.3921

C. Of Solids.—A new refractometer for measuring the refractive indices of glass plates and lenses by means of Newton's rings, is described by G. W. Royston-Pigott (*Proc. Roy. Soc.* xxiv. 393). Four kinds of glass gave the following values for mean rays:

Clear white Flint-glass	1.537
Yellow and heavy Flint-glass	1.6626
Yellowish and very heavy Flint-glass	1.723
Strong yellow, heaviest of all „	1.7555

The refractive index of collodion films (0.0081 to 0.088 mm. thick on glass plates) was found by E. Gripon (*Compt. rend.* lxxx. 882) to be 1.5108; polarising angle $56^\circ 25'$.

F. Kohlrausch (*Zeitschr. Kryst.* i. 100) has determined the following refractive indices by the method of total reflection (iii. 614):

Glass prism (at 23°):	Obsidian (at 23°)	1.4953
first face	Agate „	1.540
second face	Amber (at 21°)	1.522
by transmission	Sodium Chlorate (at 22°)	1.5145
Fluor spar:	Potash-alum, native (at 16°)	1.5461
crude, grey (at 23°)	Chrome-alum „ (at 22°)	1.481
black (at 19°)		

Refractive Power of Bodies which exhibit Anomalous* Dispersion (vii. 742).—A. Kundt (*Pogg. Ann.* cxlv. 67, 164) has determined the refractive indices of the four following anomalously dispersive liquids: (1). Cyanin, 1.22 per cent. dissolved in alcohol of sp. gr. 0.822 at 15° . (2). Cyanin, concentrated solution in the same solvent. (3). Fuchsine, not quite saturated solution in the same solvent. (4). Potassium permanganate solution not quite saturated. The first column of the following table indicates the spectral lines; e.BI and e.Gr signify the extreme blue and extreme green that could be observed on both sides of the absorption-band; in fuchsine, e.BI has nearly the position of the line F. Δa and Δw denote the differences of the refractive indices as observed in the two solvents, alcohol (a) and water (w).

The values for fuchsine, which exhibits the greatest anomaly of dispersion, are somewhat different from those determined by Christiansen (vii. 742), partly perhaps in consequence of the different degrees of purity of the substances employed, and partly of the inaccuracy of Christiansen's determination of the index n_D , as acknowledged by himself (*Pogg. Ann.* cxlvi. 154).

	Cyanin I		Cyanin II		Fuchsine		Potassium Permanganate	
	n	Δn	n	Δn	n	Δn	n	Δn
A	1.3666	—	1.3732	—	1.3818	—	1.3377	—
a	1.3678	+ 42	1.3756	+ 120	1.3845	+ 209	1.3386	—
B	1.3691	+ 49	1.3781	+ 139	1.3873	+ 231	1.3397	+ 88
C	1.3714	+ 65	1.3831	+ 182	1.3918	+ 269	1.3408	+ 91
D	—	—	—	—	1.3982	+ 315	1.3442	+ 106
e. Gr.	—	—	—	—	—	—	1.3452	—
E	1.3666	- 26	1.3658	- 34	—	—	—	—
b	1.3675	- 21	—	—	—	—	—	—
F	1.3713	+ 1	1.3705	- 7	—	—	—	—
e. Bl.	—	—	—	—	1.3613	—	1.3420	—
G	1.3757	+ 7	1.3779	+ 29	1.3668	- 82	1.3477	+ 64
H	1.3793	—	1.3821	—	1.3759	—	1.3521	+ 79

W. Wernicke (*Pogg. Ann.* clvi. 87) has determined by a peculiar method, the indices of refraction and extinction of rays which are absorbed by metallically opaque bodies. The following table gives the indices of refraction n , corresponding with the wave-lengths λ for solid fuchsine:

A	B	C	D	E	F	G	H		
$\lambda = 760$	688	656	598	589	581	571	550	532	526
$n = 1.73$	1.81	1.90	2.293	—	2.326	2.372	2.016	1.875	—
	F	G	H						
$\lambda = 522$	489	485	483	489	460	448	438	429	394
$n = 1.755$	1.593	—	1.330	1.436	1.288	1.224	1.295	1.31	1.54

The variation in the values of n justifies Kundt's theoretical views of the nature of bodies which exhibit surface colours. In silver, the indices of refraction (vii. 743) vary, between C and G $\frac{1}{2}$ H, from 4.78 to 3.18, and the experiments show—in opposition to Cauchy's theory of metallic reflection—that the coefficient of extinction is independent of the angle of incidence.

Double Refraction. The following determinations have been made by Kohlrausch (*loc. cit.*) by the method of total reflection. In the uniaxial crystals, the faces—when it is not otherwise stated—were cut at right angles to the optic axis, and the refractive indices, ω and ϵ , of the ordinary and extraordinary rays, were determined. In the biaxial crystals, the face was cut at right angles to the first median line, and, in addition to the refractive indices α and γ , the apparent angle $2E$ of the optic axes was determined, and thence the third refractive index was calculated (iii. 665):

Uniaxial Crystals.

	ω	ϵ	Temp.
Quartz	1.5438	1.5530	23°
Quartz, natural, parallel	1.5436	1.5531	24
Amethyst	1.5440	1.5533	23
Lemon Quartz, parallel	1.5444	1.5532	22
The same, parallel, axis horizontal	1.5445	—	22
Apophyllite	1.5343	1.5369	22
Potassium Ferrocyanide, natural	1.5752	1.5815	24
Calcium-copper Acetate, natural	1.436	1.478	23
The same, natural, parallel	1.435	1.478	25
Beryl, limpid, parallel	1.571	1.566	21
Beryl, " "	1.5725	1.5678	24
Beryl, greenish-blue, parallel	1.5804	1.5746	23
The same, parallel, axis horizontal	1.5803	—	22
Beryl, limpid, natural, parallel	1.573	1.568	23
Mejonite	1.5649	1.5454	22
The same	1.5657	1.5459	19
Mollite	1.5415	1.5154	21
Black Mica, natural	—	1.586	23
Sodium Nitrate	1.5842	1.3346	22
Sodium Nitrate, natural cleavage-face	1.5854	1.3369	23
Nickel Sulphate, natural	1.5099	1.4860	24

Biaxial Crystals.

	α	β	γ	Temp.	2E
Gypsum	1.5280	1.5206	1.5183	—	93.7°
Gypsum, natural cleavage	1.5289	1.5216	1.5198	26°	—
Tartaric Acid	1.6047	1.5355	1.4951	24	146.6
Citric Acid	1.5077	1.4975	1.4930	24	114.9
Adular, from the Eifel	1.5253	1.5250	1.5206	21	41.6
Adular, from the St. Gotthard	1.5246	1.5230	1.5192	21	106.7
Mica, East Indian, natural	1.5997	1.5941	1.5609	23	71.9
Aragonite	—	—	1.5301	22	—
Potassium Nitrate	1.5046	1.5031	1.5327	23	7.5
Magnesium Sulphate	1.4612	1.4553	1.4324	21	78.6
Borax	1.4712	1.4681	1.4463	23	59.0
Cupric Sulphate	1.5433	1.5368	1.5140	23	93.1
Sugar	1.5698	1.5643	1.5362	24	78.5

Optical Constants of Isomorphous Bodies.—The refractive indices, and, in the case of biaxial crystals, the angles of inclination of the optic axes, of a large number of isomorphous crystals, have been determined by Topsøe & Christiansen (*Ann. Chim. Phys.* [4], xxxi. 1), the result of which has been to confirm the main conclusion deduced by Senarmont from experiments made in 1851 (*ibid.* [3], xxxiii. 391), namely, that the optical properties of bodies are not in any way dependent upon isomorphism. In the following tables the indices of refraction are given for the Fraunhofer lines C, D, and F. The first gives these indices for single-refracting crystals. In the second table, the letters H, T, following the names of the substances, denote the crystalline system to which they belong, H = hexagonal, T = tetragonal (dimetric, quadratic, pyramidal). The positive or negative optical character of the substances in this table follows from the value of $\frac{\omega}{\epsilon}$, the ratio of the ordinary and

extraordinary refractive indices of a ray traversing the crystal at right angles to the optic axis. If $\epsilon > \omega$, this ratio is less than unity, and the crystal is optically positive; if $\epsilon < \omega$, the ratio is greater than unity and the crystal optically negative. This ratio is always to be understood as referring to the line D, except in one case, where a C is attached to it, in which it refers to the line C. The first three columns of figures contain the refractive indices, ω above and ϵ below. In the third table, containing the rhombic biaxial crystals, there are given for each substance, the three principal indices of refraction $\alpha < \beta < \gamma$ for rays which traverse the crystal parallel to the axes of optical elasticity $a > b > c$. 'Optical orientation' denotes the order in which the axes of elasticity correspond to the right-angled crystallographic axes. The sign \pm for the optical character is placed below that axis which bisects the acute angle of the two optic axes. In the monoclinic crystals included in the fourth table, the plane of the optic axes is always parallel to the plane of symmetry of the crystal. The optical orientation is determined by the angle which the line of bisection of the acute angle of the optic axes forms with the normal to the face 001 or ∞P (AB) denotes the apparent, AB the true angle of the optic axes.

I. Single-refracting Crystals.

Chemical Composition	Indices of Refraction		
	C	D	F
KBr	1.5546	1.5593	1.5715
KI	1.6584	1.6666	1.6871
NH ₄ I	1.6938	1.7031	1.7269
SiF ₄ .2NH ₄ F	1.3682	1.3696	1.3723
SnCl ₄ .2KCl	1.6517	1.6574	1.6717
Ba ² SO ₄	1.5665	1.5711	1.5825
Pb ² SO ₄	1.7780	1.7820	1.8065
Al ² (SO ₄) ₃ .K ² SO ₄ + 24H ₂ O	1.4773	1.4801	1.4868
Fe ² (SO ₄) ₃ .K ² SO ₄ + 24H ₂ O	1.4783	1.4817	1.4893
Fe ² (SO ₄) ₃ (NH ₄) ₂ SO ₄ + 24H ₂ O	1.4821	1.4854	1.4934
Mixed Alum	1.4676	1.4708	1.4772

II. *Uniaxial Crystals.*

Chemical Composition		Indices of Refraction			$n \left(\frac{\omega}{c} \right)$	Cryst. Axis
		O	D	F		
$\text{CuF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.4074 1.4062	1.4092 1.4080	1.4138 1.4124	1.0009	0.5395
$\text{NiF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.3876 1.4036	1.3910 1.4066	1.3950 1.4105	0.9889	0.5136
$\text{ZnF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.3808 1.3938	1.3824 1.3956	1.3860 1.3992	0.9905	0.5173
$\text{CoF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.3817 1.3972	— —	— —	0.9889 (C)	0.5219
$\text{MgF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.3427 1.3587	1.3439 1.3602	1.3473 1.3634	0.9880	0.5174
$\text{MnF}^2.\text{SiF}^4 + 6\text{H}^2\text{O}$	H	1.3552 1.3721	1.3570 1.3742	1.3605 1.3774	0.9875	0.5043
$\text{MgCl}^2.\text{SnCl}^4 + 6\text{H}^2\text{O}$	H	1.5715 1.583	1.5885 1.597	— —	0.9925	0.5083
KH^2PO^4	T	1.5064 1.4664	1.5095 1.4684	1.5154 1.4734	1.0280	0.6640
KH^2AsO^4	T	1.5632 1.5146	1.5674 1.5179	1.5762 1.5252	1.0325	0.6633
$(\text{NH}^4)\text{H}^2\text{PO}^4$	T	1.5212 1.4768	1.5246 1.4792	1.5314 1.4847	1.0307	0.7124
$(\text{NH}^4)\text{H}^2\text{AsO}^4$	T	1.5721 1.5186	1.5766 1.5217	1.5859 1.5296	1.0361	0.7096
$\text{K}^2\text{S}^2\text{O}^6$	H	1.4532 1.5119	1.4550 1.5153	1.4595 1.5239	0.9602	0.6416
$\text{Rb}^2\text{S}^2\text{O}^6$	H	1.4556 1.5041	1.4574 1.5078	1.4623 1.5167	0.9666	0.6307
$\text{CaS}^2\text{O}^6 + 4\text{H}^2\text{O}$	H	1.5463	1.5496	1.5573	—	1.500
$\text{SrS}^2\text{O}^6 + 4\text{H}^2\text{O}$	H	1.5266 1.5232	1.5296 1.5252	1.5371 1.5312	1.0029	1.5024
$\text{PbS}^2\text{O}^6 + 4\text{H}^2\text{O}$	H	1.6295 1.6492	1.6351 1.6531	1.6481 1.6666	0.9891	1.4696
$\text{NiSO}^4 + 6\text{H}^2\text{O}$	T	1.5078 1.4844	1.5109 1.4873	1.5173 1.4930	1.0159	1.9062
$\text{NiSeO}^4 + 6\text{H}^2\text{O}$	T	1.5357 1.5089	1.5393 1.5125	1.5473 1.5196	1.0177	1.8364
$\text{ZnSeO}^4 + 6\text{H}^2\text{O}$	T	1.5255 1.5004	1.5291 1.5039	1.5367 1.5108	1.0168	1.8949
$\text{BeSO}^4 + 4\text{H}^2\text{O}$	T	1.4691 1.4374	1.4720 1.4395	1.4779 1.4450	1.0226	0.9461

III. Rhombic Baxial Crystals.

Chemical composition	Indices of Refraction		Orientation	Angle of Optic axes	Axes of Elasticity	Crystallographic axes
	C	D	F			
$\text{Li}_2\text{SO}_4 + 2\text{H}_2\text{O}$	1.5462	1.5487	1.5548	a c b ⊥	AB = 78° 16' (AB) = 159° 40' AB _c = 33° 21' AB _F = 28° 6' (AB) _K = 56° 48' (AB) _F = 47° 59'	1 : 0.9809 : 0.9934
	1.5763	1.5788	1.5887			
	1.5565	1.5602	1.5680			
$\text{Ag}_2\text{SO}_4 + 2\text{H}_2\text{O}$	1.6272	—	1.6404	a c b	1 : 0.9802 : 0.9819	1 : 0.9850 : 0.9802
	1.6601	—	1.6770			
	1.6573	—	1.6748			
K_2SO_4	1.4911	1.4932	1.4976	a c b +	AB = 67° 4' (AB) = 111° 19'	1 : 0.7404 : 0.5727
	1.4939	1.4980	1.5029			
	1.4928	1.4946	1.4992			
K_2SeO_4	1.5323	1.5353	1.5417	a c b +	AB = 76° 40' (AB) = 145° 32'	1 : 0.7296 : 0.5724
	1.5422	1.5450	1.5523			
	1.5373	1.5402	1.5475			
K_2CrO_4	—	—	—	a c b	AB = 51° 40' (AB) = 97° 30'	1 : 0.7297 : 0.5695
	—	—	—			
	1.7131	1.7254	1.7703			
$\text{MnSeO}_4 + 2\text{H}_2\text{O}$	$\mu_c - \mu^b$	= 0.123	—	c a b	(A'B') _b = 130° 30'	1 : 0.9959 : 0.8849
$\text{CdSeO}_4 + 2\text{H}_2\text{O}$	$\mu_c - \mu^b$	= 0.089	—	c a b	(A'B') _b = 131° 2'	1 : 0.9753 : 0.8764
$\text{BaSO}_4 + 4\text{H}_2\text{O}$	1.4992	1.5027	1.5101	c b a	AB = 26° 48' (AB) = 40° 43'	1 : 1.0129 : 1.0248
	1.4973	1.5007	1.5084			
	1.4639	1.4667	1.4725			

III. *Rhombohedral Crystals.*

Chemical composition	Indices of Refraction			Orientation	Angle of Optic axes. \angle	Axes of Elasticity	Crystallographic axes
	C	D	F				
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	—	1.4469	1.4729	$\left. \begin{matrix} a & c & b \\ - & - & - \end{matrix} \right\}$	AB = $41^\circ 56'$ (AB) = $64^\circ 22'$	1 : 0.9830 : 0.9852	1 : 0.9815 : 0.5656
	—	1.4921	1.4981				
	—	1.4888	1.4949				
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	1.4544	1.4568	1.4620	$\left. \begin{matrix} a & c & b \\ - & - & - \end{matrix} \right\}$	AB = $46^\circ 14'$ (AB) = $71^\circ 3'$	1 : 0.9819 : 0.9843	1 : 0.9804 : 0.5631
	1.4812	1.4836	1.4897				
	1.4776	1.4801	1.4860				
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	1.4305	1.4325	1.4374	$\left. \begin{matrix} a & c & b \\ - & - & - \end{matrix} \right\}$	AB = $51^\circ 25'$ (AB) = $78^\circ 18'$	1 : 0.9806 : 0.9843	1 : 0.9901 : 0.5709
	1.4583	1.4608	1.4637				
	1.4530	1.4554	1.4607				
$\text{MgCrO}_4 \cdot 7\text{H}_2\text{O}$	1.5131	1.5211	—	$\left. \begin{matrix} a & c & b \\ - & - & - \end{matrix} \right\}$	AB = $75^\circ 28'$ (AB) = $143^\circ 6'$	1 : 0.9701 : 0.9814	1 : 0.9901 : 0.5735
	1.5633	1.5680	—				
	1.5415	1.5500	—				
$\text{K}_2\text{SO}_4 \cdot \text{C}_2\text{H}_4\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$	1.6306	1.6360	1.6497	$\left. \begin{matrix} b & a & c \\ - & - & - \end{matrix} \right\}$	AB = $42^\circ 34'$ (AB) = $72^\circ 50'$	1 : 1.0099 : 0.9991	1 : 0.9049 : 0.8645
	1.6148	1.6199	1.6325				
	1.6322	1.6375	1.6511				
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{C}_2\text{H}_4\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$	n_a 1.6229	—	—	$\left. \begin{matrix} b & a & c \\ - & - & - \end{matrix} \right\}$	AB = $68^\circ 8'$ (AB) = $130^\circ 46'$	—	1 : 0.9259 : 0.8261
	1.5168	1.5188	1.5279				
	1.5577	1.5614	1.5689				
$(\text{NH}_4)\text{HCO}_3$	1.5861	1.5910	1.6000	$\left. \begin{matrix} a & b & c \\ - & - & - \end{matrix} \right\}$	AB = $79^\circ 54'$ (AB) imaginary	1 : 0.9727 : 0.9546	1 : 0.7086 : 0.6983

IV. Monoclinic Biaxial Crystals.

Chemical composition	Indices of Refraction		F	Orientation	Angle of Optic axes	Crystallographic axes
	C	D				
$\text{MgSeO}_4 \cdot 6\text{H}_2\text{O}$	1.4864	1.4856 1.4892 1.4911	1.4965	$\bar{a} \ b \ (001) = 35^\circ 36'$	$\begin{matrix} AB = 28^\circ 12' \\ (AB) = 42^\circ 33' \end{matrix}$	$\left. \begin{matrix} 1.3853 : 1 : 1.6850 \\ 81^\circ 28' \end{matrix} \right\}$
$\text{CeSeO}_4 \cdot 6\text{H}_2\text{O}$	1.5183	1.5225 1.5227	—	$\bar{a} \ b \ (001) = 42^\circ 56'$	$\begin{matrix} AB = 71^\circ 3' \\ (AB) = 11^\circ 0' \end{matrix}$	$\left. \begin{matrix} 1.3709 : 1 : 1.6816 \\ 81^\circ 46' \end{matrix} \right\}$
$\text{NiSeO}_4 \cdot \text{K}_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5207	1.5199 1.5218 1.5339	1.5315	$(001) \ b \ c = 83^\circ 3'$	$\begin{matrix} AB = 72^\circ 56' \\ (AB) = 129^\circ 56' \end{matrix}$	$\left. \begin{matrix} 0.7454 : 1 : 0.5060 \\ 75^\circ 7' \end{matrix} \right\}$
$\text{CoSeO}_4 \cdot \text{K}_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5162	1.5135 1.5195 1.5356	2.5270	$(001) \ b \ c = 86^\circ 35'$	$\begin{matrix} AB = 63^\circ 52' \\ (AB) = 106^\circ 58' \end{matrix}$	$\left. \begin{matrix} 0.7369 : 1 : 0.5056 \\ 75^\circ 50' \end{matrix} \right\}$
$\text{ZnSeO}_4 \cdot \text{K}_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5148	1.5115 1.5177 1.5327	1.5252	$(001) \ b \ c = 88^\circ 19'$	$\begin{matrix} AB = 66^\circ 8' \\ (AB) = 111^\circ 50' \end{matrix}$	$\left. \begin{matrix} 0.7441 : 1 : 0.5075 \\ 75^\circ 46' \end{matrix} \right\}$
$\text{MgSeO}_4 \cdot \text{K}_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.4942	1.4950 1.4970 1.5120	1.5039	$(001) \ b \ c = 88^\circ 0'$	$\begin{matrix} AB = 40^\circ 2' \\ (AB) = 62^\circ 12' \end{matrix}$	$\left. \begin{matrix} 0.7447 : 1 : 0.5014 \\ 75^\circ 43.5' \end{matrix} \right\}$
$\text{CuSeO}_4 \cdot \text{K}_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5203	1.5096 1.5335 1.5387	1.5320	$\bar{a} \ b \ (001) = 2^\circ 26'$	$\begin{matrix} AB = 88^\circ 12' \\ (AB) \text{ imaginary} \end{matrix}$	$\left. \begin{matrix} 0.7489 : 1 : 0.5230 \\ 76^\circ 41' \end{matrix} \right\}$
$\text{NiSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5334	1.5201 1.5312 1.5466	1.5441	$(001) \ b \ c = 73^\circ 6'$	$\begin{matrix} AB = 86^\circ 14' \\ (AB) \text{ imaginary} \end{matrix}$	$\left. \begin{matrix} 0.7378 : 1 : 0.5042 \\ 73^\circ 41' \end{matrix} \right\}$

IV. Monoclinic Biaxial Crystals.

Chemical composition	Indices of Refraction		Orientation	Angle of Optic axes	Crystallographic axes
	C	D			
$\text{CoSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5280	1.5246 1.5311 1.5396	(001) $b \pm c = 76^\circ 18'$	AB = $82^\circ 1'$ (AB) imaginary	$\left. \begin{array}{l} 0.7414 : 1 : 0.5037 \\ 73^\circ 37' \end{array} \right\}$
$\text{MgSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5046	1.5056 1.5075 1.5150	(001) $b \pm c = 72^\circ 53'$	AB = $53^\circ 44'$ (AB) = $85^\circ 56'$	$\left. \begin{array}{l} 0.7414 : 1 : 0.4968 \\ 73^\circ 23' \end{array} \right\}$
$\text{ZnSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5259	1.5233 1.5292 1.5372	(001) $b \pm c = 76^\circ 56'$	AB = $81^\circ 22'$ (AB) = $171^\circ 20'$	$\left. \begin{array}{l} 0.7416 : 1 : 0.5062 \\ 73^\circ 49' \end{array} \right\}$
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5177 1.5226 1.5339	1.5201 1.5260 1.5356	(001) $b \pm c = 80^\circ 37'$	AB = $76^\circ 48'$ (AB) = $142^\circ 50'$	$\left. \begin{array}{l} 0.7405 : 1 : 0.5012 \\ 73^\circ 47' \end{array} \right\}$
$\text{CuSeO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.5317	1.5213 1.5355 1.5395	a b (001) = $31^\circ 2'$	AB = $55^\circ 24'$ (AB) = $91^\circ 6'$	$\left. \begin{array}{l} 0.7488 : 1 : 0.5126 \\ 74^\circ 27.5' \end{array} \right\}$
$\text{MgSO}_4 \cdot (\text{NH}_4)_2\text{SeO}_4 + 6\text{H}_2\text{O}$	1.4698 1.4707 1.4751	1.4717 1.4728 1.4791	(001) $b \pm c = 78^\circ 49'$	AB = $50^\circ 40'$ (AB) = $78^\circ 4.5'$	$\left. \begin{array}{l} 0.7376 : 1 : 0.4891 \\ 72^\circ 54' \end{array} \right\}$
$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$	1.4582 1.4610 1.4743	1.4602 1.4633 1.4768	(001) $b \pm c = 89^\circ 30'$	AB = $48^\circ 41'$ (AB) = $73^\circ 5'$	$\left. \begin{array}{l} 0.7420 : 1 : 0.5005 \\ 75^\circ 5' \end{array} \right\}$
$\text{FeSO}_4 \cdot \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$	1.4751 1.4806 1.4947	1.4775 1.4832 1.4973	(001) $b \pm c = 86^\circ 16'$	AB = $67^\circ 18'$ (AB) = $110^\circ 32'$	$\left. \begin{array}{l} 0.7512 : 1 : 1.5111 \\ 75^\circ 44' \end{array} \right\}$

Double Refraction of Various Substances.—Mercurous iodide, Hg_2I_2 , which Des Cloizeaux has shown to be isomorphous with mercuric iodide (*Compt. rend.* lxxxiv. 1418), is likewise strongly double-refracting; it is uniaxial and positive, whereas mercuric iodide is negative. Mercurous chloride is also positive.

Cupric Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The optical constants of this salt have been determined by C. Pape (*Pogg. Ann.* vi. 35; *Jahresb. f. Chem.* 1873, 137). The three principal refractive indices for sodium light (D) are:

$$\alpha = 1.51564 \quad \beta = 1.53940 \quad \gamma = 1.54639$$

The dispersion is small, as shown by the following values:

	D	E	F	G
for the lines α	1.51615	1.51983	1.52307	1.52872
γ	1.54604	1.54996	1.55351	1.55978

The angles between the optic axes are slightly diminished by rise of temperature, about $12.1'$ for a rise from 19.1° to 46.7° .

Cane-sugar. The three principal refractive indices, and the angles $2V$ of the optic axes for the sodium, lithium, and thallium lines, have been determined by L. Calderon (*Zeitschr. Kryst.* i. 73):

	α	β	γ	$2V$
Li . . .	1.5379	1.5638	1.5693	$47^\circ 56'$
Na . . .	1.5397	1.5667	1.5716	$48^\circ 0'$
Tl . . .	1.5422	1.5685	1.5734	$48^\circ 08'$

The dispersion of the median lines is almost nothing; that of the optic axes is weak.

F. Becke (*Min. Mittheil.* vii. 261) finds that for sodium light, the crystallographic axis c is inclined to the smallest optic axis at an angle of $23^\circ 23'$. For sodium-light, and for light which has passed through red and green monochromatic glasses respectively, he finds the following values for the refractive indices and the angle of the optic axes:

	α	β	γ	$2V$
Red . . .	1.5351	1.5630	1.5679	$47^\circ 42' 30''$
Yellow . . .	1.5371	1.5653	1.5705	$47^\circ 48' 20''$
Green . . .	1.5404	1.5687	1.5737	$47^\circ 57' 56''$

Terpin Hydrate, $\text{C}^{10}\text{H}^{16} \cdot 3\text{H}_2\text{O}$. This compound forms orthorhombic crystals having the axial ratio $a : b : c = 0.80722 : 1 : 0.47640$. The plane of the optic axes coincides with ∞P ; the first median line with the brachydiagonal a . The angle of the optic axes is for lithium-light $77^\circ 37'$; for sodium-light $77^\circ 27'$; for thallium-light $77^\circ 18'$; the dispersion of the optic axes is therefore very small (Arzruni, *Pogg. Ann.* clii. 282).

Influence of Temperature on the Refractive Indices of the Isomorphous Sulphates of Barium, Strontium, and Lead (Heavy Spar, Cælestine, and Anglesite).—1. The three principal indices of refraction of these three sulphates vary, with change of temperature, by different amounts, but always decrease in magnitude as the temperature rises. 2. This decrease in the three compounds is analogous in so far that the largest index (γ) suffers the greatest, and the medium index (β) the smallest amount of diminution. 3. In anglesite the refractive power diminishes with rise of temperature, but the dispersion increases. 4. The directions of the principal axes of expansion by heat do not stand in any direct relation to the magnitude of the axes of optic elasticity (Arzruni, *Zeitschr. Kryst.* i. 165).

Development of Double-refracting Structure by Electric Induction.—Isotropic media, solid or liquid, submitted to strong electric inductive action, become doubly refractive, their particles being apparently arranged in the direction of the lines of magnetic force. The structure thus acquired is uniaxial, the axis being parallel to the lines of force. Glass and quartz become positively double-refracting, resin negatively. Among liquids, carbon disulphide, benzene, paraffin, kerosene oil, and turpentine oil become positive, olive oil negative. Carbon disulphide acquires the strongest, paraffin oil and kerosene oil the weakest double refraction. In solid bodies, the development of double refraction by electric influence, takes a perceptible time (up to half a minute) and an equal time is required for its disappearance after the electric force has ceased to act; in liquids both the production and the disappearance of the double refraction are instantaneous (J. Kerr, *Phil. Mag.* [4], i. 337, 446).

Fluorescence. The fluorescence of a large number of substances has been examined by E. Hagenbach (*Pogg. Ann.* cxlvi. 65, 232, 375, 508; *abstr. Chem. Soc. Jour.* xxv. 1058), with results confirming in every instance the two laws discovered

by Stokes, viz. (1) that the fluorescent rays are always less refrangible than the exciting rays; (2) that the same rays which are capable of producing fluorescence within a substance are also absorbed by that substance.

Light of every degree of refrangibility appears to be capable of exciting fluorescence, which, in the more refrangible part, extends beyond the line H, being there produced by lowering of refrangibility of the ultra-violet rays; on the other hand, any fluorescent light that might be produced by the extreme red rays, would, for obvious reasons, not be perceptible to our eyes. The number of maxima of fluorescence in the spectrum is very different for different substances; thus Hagenbach, by examining the spectrum of an illuminated slit, the light of which was thrown on different liquids, observed

7	maxima in a fresh solution of chlorophyll	
6	" in an altered solution of chlorophyll	
5	" in an extract of lamp-black	
4	" in barium platinocyanide	
3	" in naphthalene-red	} and in other substances.
2	" in oxidised brazilin	
1	" in the solution of marin-alumina	

Stokes's observation that the absorption-bands of fluorescent bodies correspond generally with the maxima of fluorescence has been confirmed by Hagenbach in nearly all cases, a few bodies in which absorption is not accompanied by fluorescence being, perhaps, mixtures of a fluorescent and a non-fluorescent substance. Uranic nitrate, however, which exhibits no maxima of fluorescence either in the solid state or in solution, seems to form a real exception to the rule, since it can scarcely be looked upon as a mixture.

The maxima of fluorescence in the spectrum of a body do not always correspond with those in the spectrum of the fluorescent light, or *fluorescence spectrum*; the solution of chlorophyll, for example, shows seven maxima of fluorescence in its spectrum, but only two in that of the fluorescent light.

The position of the maxima and minima of fluorescence vary more or less with the nature of the solvent employed, and some substances exhibit fluorescence only in one state of aggregation, whereas others are fluorescent both in the solid and in the liquid state.

Further experiments by Hagenbach (*Pogg. Ann.* Jubelbd. 1874, 303) have yielded the following results: A comparison of the fluorescence spectra of the alcoholic and ethereal extracts of chlorophyll shows that the maxima in the former are placed nearer to the red end than in the latter, and that the minimum between the two maxima is more distinct in the ethereal than in the alcoholic extract. Chlorophyll likewise exhibits fluorescence in the solid state, though not so strongly as when dissolved, the spectrum of the solid substance being less extended and notably displaced towards the side of lesser refrangibility.

The fluorescence-spectrum of solid anthracene exhibits seven maxima. The blue-violet fluorescence solutions of this substance in alcohol, ether, and light petroleum exhibit the displacement of the maxima towards the violet end, previously observed by Morton (p. 93 of this volume). Hagenbach, however, attributes the spectrum with six or seven maxima to pure anthracene, whereas Morton supposed that it was due to the presence of chrysogen. Hagenbach did not observe any absorption-bands in the spectrum of pure anthracene.

Thallene, a greenish-brown hydrocarbon discovered by Morton in petroleum-residues (*Chem. News*, xxvi. 272), exhibits a fluorescence very much like that of anthracene. Solid thallene exhibits no absorption-bands except those which are due to its splendid green fluorescence; its two spectra are exactly complementary one to the other. In all its solutions it exhibits a strong blue fluorescence, and all its bands appear displaced towards the more refrangible end of the spectrum in various degrees according to the solvent used. Prolonged insolation and rise of temperature give rise to the gradual disappearance of the fluorescence-bands from the red end onwards (*Morton, Phil. Mag.* [4], xlii. 89).

The fluorescence and absorption-spectrum of chrysene, both solid and in solution, is also very much like that of anthracene. Solid chrysene exhibits 4, dissolved chrysene 5 maxima in its fluorescence-spectrum, their arrangement being modified by the solvent (chloroform, benzene, turpentine-oil, ether). Two or three absorption-bands were also observed. Insolation displaces the maxima of solid chrysene in the direction of greater refrangibility, and develops a fifth maximum (*Morton, Amer. Chemist*, v. 115).

Ordinary white paper exhibits a whitish fluorescence, which is, moreover, continuous after the removal of the exciting rays, and has therefore the character of phosphorescence; it begins at the line *b*, attains its maximum at *G*, and extends to

the ultra-violet. This fluorescence-spectrum exhibits two rather strong maxima separated by a minimum (Hagenbach).

Hagenbach has also examined the fluorescence of the *platinocyanides* of the following metals:

Potassium	Strontium
Sodium	Strontium-potassium
Potassium-sodium	Calcium
Ammonium	Calcium-potassium
Sodium-ammonium	Magnesium
Barium	

The fluorescent appearances of these salts are very diversified, as each yields several hydrates differing both in their body-colour and in their fluorescence. The body-colour is determined chiefly by the rays which excite fluorescence. Most of these salts exhibit very fine surface-colours.

Ch. Horner (*Phil. Mag.* [4], xlviii. 165) recommends castor-oil as a solvent for fluorescent bodies which do not exhibit this property when dissolved in other liquids. Red indigo (Persio) dissolved in this oil exhibits a splendid orange fluorescence; camwood apple-green; logwood a similar colour but with a different spectrum; turmeric, emerald-green, at least three times as strong as in the alcoholic extract.

E. Lommel (*Pogg. Ann.* cxliii. 26; clxx. 514) infers, from observations on various fluorescent substances, that Stokes's law respecting the relative refrangibilities of the exciting and fluorescent rays is not universally true. His conclusions are as follows: (1). There are two kinds of fluorescence. In the first, each homogeneous exciting ray, which, as regards its refrangibility, falls within the limits of the fluorescence-spectrum, or a certain portion of it, is capable of exciting not only rays of greater or of equal wave-length, but also rays of lesser wave-length, so far as they are included within the same limits. In the second kind of fluorescence each homogeneous exciting ray produces only those rays of fluorescent light whose wave-lengths are greater or at least equal to its own. (2). In bodies which exhibit the first kind of fluorescence, such as naphthalene, chlorophyll, and iron, each exciting homogeneous ray calls into existence the entire fluorescence-spectrum: these bodies therefore do not conform to Stokes's law. (3). Most of the fluorescent bodies hitherto examined exhibit only the second kind of fluorescence, and therefore obey Stokes's law throughout the extent of their fluorescence-spectra. (4). There are also bodies which exhibit both kinds of fluorescence, the first in a certain part of their fluorescence-spectrum, the second kind in the remainder; these, therefore, conform partially to Stokes's law. Such are Griessmayer's chameleon-red, chameleon-blue, and chameleon-green produced by heating aniline hydrochloride with azobenzene (see PHENYL COLOURING MATTERS).

According to Hagenbach (p. 1194) and Lubarsch (*Pogg. Ann.* cxliii. 420), on the other hand, the relation between the wave-lengths of the exciting and fluorescent rays is in all cases represented by Stokes's law. Lubarsch also infers from his own experiments: (1). That the fluorescence of each substance can be developed only by certain exciting rays. (2). That the most refrangible rays of the fluorescent light excited by sunlight correspond with the position of maximum absorption, provided that the fluorescence is *simple*. Various bodies, however (e.g. extract of Palisander wood, an ethereal solution of archil, and alcoholic tincture of litmus), exhibit a *double* or *multiple fluorescence*, due to the action of various groups of rays of the exciting light. Chlorophyll belongs to this class of bodies, but is probably a mixture of several substances, each of which exhibits only simple fluorescence.

Fluorescence, Phosphorescence and Absorption Spectra of Uranium Solutions.*—The light emitted by phosphorescent uranium compounds has been spectroscopically examined by E. Becquerel (*Ann. Chim. Phys.* [4], xxvii. 539). The experiments were made in some cases with the aid of Becquerel's phosphoscope † (*ibid.* [3], lvii. 101), while in others the bodies were illuminated exclusively by the violet and ultra-violet rays. Uranous chloride and sulphate thus treated do not emit any sensible light. Most uranic compounds, on the other hand, become phosphorescent, and almost all of them then give a series of groups of light and dark bands between C and F. The order of the bands in the several groups is determined chiefly by the acid present in the compound, and exhibits great diversity. In the double salts of any particular class, the double sulphates for example, the order in each group is the same, but the

* Phosphorescence is fluorescence continuing after the removal of the exciting cause.

† This is an instrument for facilitating the detection of phosphorescence in bodies which exhibit it for a very short time only. For description and figures, see E. Becquerel (*La Lumière, ses causes et ses effets*, i. 249, 334, 378; *Ann. Chim. Phys.* [3], lvii. 101; also *Traité de Physique* par A. Daguin, iv. 252).

index of refraction of the corresponding light and dark bands varies sometimes in one direction, sometimes in the opposite. In each individual spectrum the distance between the corresponding maxima and minima of light of the successive groups increases with the refrangibility. The differences of the corresponding wave-lengths divided by the square of the mean wave-length give quotients which are nearly equal for all uranium compounds. On the other hand, no simple relation could be discovered between the wave-lengths of homologous bands of the same group in different compounds and their chemical composition. When the compounds are illuminated by violet and ultra-violet light, the more refrangible part of the spectrum exhibits additional groups of absorption-bands, which are different in different compounds, and agree in their order of succession with those in the less refrangible part of the spectrum, appearing, indeed, like a continuation of the latter.

Becquerel's results have been confirmed by Morton A. Bolton (*American Chemist*, iii. 361, 401), whose observations extend to a larger number of uranium salts. They find that, whereas in the spectra of all these salts the similar and similarly distributed bands of the fluorescent light are situated between the lines C and F, there are also other absorption-bands situated between F and H, which are not due to fluorescence, but are, nevertheless, similar to those above mentioned, and somewhat regularly distributed. The intensity curves of the spectra exhibit characteristic differences between different salts, and may serve to distinguish them one from the other. In all cases the intensity of the bands decreases more quickly in one direction than in the opposite, and, for the most part, more quickly towards the more refrangible end. The character of one band is, for the most part, a type of all the bands in the same spectrum; exceptions to this rule are, however, afforded by most of the double acetates, especially sodio-uranic acetate. Double salts containing the same acid have in most, but not in all cases, bands of the same type; but simple and double salts of the same acids do not, for the most part, agree in the type of their bands. In many cases an internal decomposition of a salt by heat could be distinctly traced by the spectroscope. Thus when hydrated ammonio-uranic sulphate, $\text{U}^{\text{O}}\text{SO}_3(\text{NH})^2\text{OSO}_3 + 2\text{H}_2\text{O}$, is heated, it is first converted into the anhydrous salt, and finally into a new salt, containing less ammonia, viz. $2\text{U}^{\text{O}}\text{SO}_3(\text{NH})^2\text{OSO}_3$. The spectra of the three salts are similar, but are distinguished from one another by the arrangement and relative intensities of their bands. When the original hydrate is slowly heated, the spectrum of the anhydrous salt at first accompanies that of the hydrate, and with continually increasing intensity, while that of the hydrate gradually fades. The passage from the hydrate to the new double salt is accompanied by similar appearances.

The absorption-spectra of many uranic salts exhibit great diversities, the character of the absorption-bands being in many cases greatly influenced by the fluorescence, in others but slightly. The acetates, simple and double, which in the solid state give very different absorption-spectra, exhibit in solution almost exactly similar spectra, so that it may be inferred, with great probability, that double uranic acetates cannot exist in solution, but are decomposed in the act of dissolving. Different solvents displace the bands in various degrees.

Fluorescence is diminished by heat. In anhydrous ammonio-uranic sulphate the fluorescence is considerably weakened at 140° and destroyed at 260° . In sodio-uranic acetate all the fluorescence-bands disappear at 116° , and during the heating the bands are somewhat displaced towards the red end; as the salt cools, the optical phenomena regain their original character. Salts in solution lose their fluorescence at lower temperatures than in the solid state. Many uranic salts, especially the carbonates, exhibit, when heated, a downward displacement (? towards the red end) of their absorption-bands; others, especially the nitrates, and likewise the acetates, exhibit, when heated, not a displacement of the bands, but a distinct diminution of the general absorption.

Illumination of Transparent Bodies.—Lallemand's observations on this subject (vii. 745) have been continued (*Compt. rend.* lxxvii. 1216) with the following results: The rays which produce the illumination of transparent bodies are of two kinds:—those of the one kind, resulting from a direct lateral propagation of the incident light, have a wave-length equal to that of the latter, and are partly or completely polarised, according as the incident light is natural or polarised; while those of the other kind are always unpolarised, and often of less refrangibility than the original light: these are the rays which in transparent bodies produce fluorescence, and in opaque substances, body-colour. Fluorescence may be regarded as a universal property of bodies, being exhibited, even by the purest liquids, as, for example, sulphur dioxide or cyanogen condensed by pressure. The only bodies which are distinctly illuminated without fluorescing are perfectly pure quartz and rock-salt. Calc spar exhibits a reddish-orange fluorescence, somewhat brighter and of a deeper red with the ordinary than with the extraordinary ray; isochromatic illumination (vii. 745), however, is scarcely

perceptible in this substance. Colourless fluorspar exhibits both properties in a high degree; its fluorescence is of a violet-indigo colour. Pure naphthalene dissolved in alcohol gives a bright indigo-blue fluorescence, the spectrum of which shows all the colours, but most conspicuously the rays between F and G. When polarised light falls on glass which has been quickly cooled, the glass emits at certain points white partially polarised light, at others unpolarised light of yellowish-green or bluish-green colour, according to the fluorescence of the particular kind of glass. This effect is connected with the double refraction resulting from the internal tension of the particles.

Illumination of Opaque Bodies and External Diffusion.—The light scattered from the surfaces of these bodies consists of three parts: 1. That resulting from true diffusion, which obeys the same laws as the inner diffusion or illumination of transparent bodies. 2. That which is due to true reflection from the inequalities of the surface. 3. That which is due to fluorescence. Lamp-black is the substance in which the reflection is of smallest amount, indeed almost evanescent; nevertheless, this substance exhibits a faint yellowish fluorescence. In most other black substances the predominant appearance is reflection, most conspicuously in platinum-black. The number of really black bodies, that is to say of bodies which reflect and diffuse no coloured light, but only a faint white light, is, however, smaller than is commonly supposed, many apparently black precipitates, for example, exhibiting distinct colours when dried and spread out in thin layers; thus the sulphide and phosphide of copper are greenish-brown; lead sulphide and silver sulphide are bluish-grey, &c. Actually black are the following: well-washed aniline-black; mercury sulphide obtained by the action of hydrogen sulphide on mercuric chloride; uranium oxide, U_2O_5 ; cupric oxide precipitated from the nitrate by lime; platinum-black; iron reduced by hydrogen; finely pulverised arsenic oxidised by exposure to the air (Lallemand, *Ann. Chim. Phys.* [5], viii. 93).

Relations between Absorption and Dispersion in Mixtures.—When an ordinary transparent medium, whose refractive power n is related to the wave-length λ in the manner represented by the equation $n = a + \frac{b}{\lambda^2}$ is mixed with a strongly

absorbing body, the absorption-bands of the mixture are in most cases displaced towards the red end of the spectrum, the displacement increasing with the value of b . This relation throws light on the hitherto obscure observations regarding the influence of solvents on absorption (e.g. in the chlorophyll spectrum); also on the observations made by Melde in 1865 (*Pogg. Ann.* cxxiv. 91; cxxvi. 265; *Jahresb.* 1865, 85) on the displacement and occasional disappearance of the absorption-bands of a substance consequent on the presence of another which does not act chemically on it, but is likewise capable of producing absorption-bands (Kundt, *Pogg. Ann.* Jubelbd. 615).

On the relations between the absorptive powers of Coloured Bodies in the Solid State and in Solution, see W. Ackroyd (*Chem. News*, xxxvi. 159).

Instruments for the observation of Absorption in Solutions are described by G. Govi (*Compt. rend.* lxxxv. 1046; *Jahresb. f. Chem.* 1877, 184).

On Absorption-spectra, see SPECTRAL ANALYSIS.

Colours of Bodies. The change of colour produced in bodies by heat, on which observations were made a few years ago by Houston (vii. 746), has been further investigated by W. Ackroyd (*Chem. News*, xxxiv. 75; *Phil. Mag.* [5], ii. 423; *Chem. Soc. Jour.* xxxi. 571), who designates it by the term *Metachromatism*. The colours were spectroscopically examined after the light had passed through a thin layer of the pulverised substance. Heating usually produces (as may be seen in the case of potassium dichromate) a contraction of the transmitted portion of the spectrum, in greater proportion towards the more refrangible than towards the less refrangible side, whereby a change of colour is produced in the direction of the red, which is, in fact, the general law of colour-change produced by heat. The series of colours must, however, be extended beyond the red to include brown and black, and beyond the violet to include white (or colourless). In a series of anhydrous binary compounds of the same two elements, those which contain the largest proportion of metal have the most refrangible, and those which contain the smallest proportion of metal have the least refrangible, colours. Metachromatism occurs in all states of aggregation; it is not necessarily connected with rise of temperature or with alteration of density, and may therefore be produced by increase or decrease of distance between the atoms within the molecule, in other words, with alteration of the atomic potential. A change from the white (violet) to the black (red) extremity of the spectrum indicates a separation of the atoms, the contrary change an approximation. If the alteration of the potential proceeds as far as chemical action, the former change of colour denotes combination, the second decomposition.

Dichroism.—The double-refracting orthorhombic crystals of iodine are dichroic in consequence of unequal absorption, appearing dark red or brownish yellow according to the direction in which they are viewed. The optic axis of the rhombic plates is parallel to the macrodiagonal. The ray polarised parallel to this axis suffers less absorption than that which is polarised at right angles thereto. The reflected light is polarised partly at right angles to the transmitted light, partly parallel to the plane of incidence. If the incident light is polarised parallel to the plane of incidence, and the angle of incidence is about 72° , the reflected light is of a bright blue colour, complementary to the transmitted light (Sir John Conroy, *Proc. Roy. Soc.* xxv. 51).

The absorption-spectra of iodine in the solid and fused states are nearly identical, and consist only of the red portion to a little short of D, beyond which absorption takes place very rapidly in fused, more slowly in solid iodine. The solutions, as formerly observed by Schultz-Sellack (vii. 672), are either red-brown or violet. To the former class belong the solutions in alcohol, ether, ethyl bromide, ethylene chloride, benzene, glycerin, aqueous potassium iodide, hydrochloric acid, &c.: they absorb the spectrum from the violet end to about the middle between D and E; to the latter, the solutions in disulphide, tetrachloride, and monochloride of carbon, chloroform, phosphorus trichloride, stannic chloride, and hot concentrated sulphuric acid: these solutions strongly absorb the rays of medium refrangibility, and their spectrum resembles that of iodine-vapour (vii. 672). In thin layers, or when somewhat dilute, they appear red; in thicker layers violet, because the violet rays are still transmitted after the red have been absorbed (Conroy, *Proc. Roy. Soc.* xxv. 46). The dichroism of iodine in alcoholic solution has also been observed by Andrews (*Chem. News*, xxiv. 75).

Temporary dichroism may be produced by tension in caoutchouc and gutta-percha, and in a slight degree in gelatin which has been made extensible by addition of glycerin and coloured by certain dye-stuffs (A. Kundt, *Pogg. Ann.* cli. 125).

Elliptic Polarisation and Surface-colours.—E. Wiedemann (*Pogg. Ann.* cli. 1) has determined the relation between the angle of incidence and the phase of retardation of the reflected ray (iii. 659) for five spectral colours, from reflecting surfaces of fuchsine, aniline-violet, and copper. Strong elliptic polarisation was observed also in light reflected from a concentrated solution of fuchsine. The changes of colour exhibited by bodies with surface-colour in contact with media of different refrangibility—first observed by Haidinger (*Wien. Akad. Ber.* viii. 97; *Jahresb. f. Chem.* 1852, 162), have been further studied by Wiedemann, whose experiments show that the surface-colour varies enormously according to the nature of the medium in contact with the body, and that the changes of colour in the light reflected from double-refracting crystals according to the inclination of the reflecting surface to the axis of the crystals—also studied by Haidinger (*Pogg. Ann.* lxxi. 321; *Jahresb.* 1847–48, 194)—are independent of any particular arrangement of the surface-particles. Amongst the relations brought to light by this investigation, the following may be especially mentioned: (1) That the colours most strongly reflected (in air) likewise exhibit the strongest elliptic polarisation; and (2) That the principal angle of incidence, or polarising angle (whose tangent is the index of refraction, iii. 653), is subject to the most rapid variations for wave-lengths nearly corresponding with absorption-bands (*comp.* Kundt, vii. 744). Semi-metallic bodies, in regard to the phases of retardation of light which falls upon them, behave like transparent bodies for the rays which they transmit, and like metals for those which they reflect.

II. CIRCULAR POLARISATION.*

Polarimeters, or Polaristrobometers (from *στροβος*, rotation).—**Saccharimeters.** Besides the Soleil Saccharimeter, a number of other instruments are now in use for determining the rotatory power of optically active substances, and may here be briefly described.

Soleil-Duboseq Saccharimeter.—The Soleil saccharimeter now manufactured by Duboseq of Paris is in all essential features identical with that already described (vol. iii. 674); the regulator *ni* (fig. 697, vol. iii. 674) is placed, however, at the eye-piece end of the instrument instead of behind the polariser *c*,† as will be evident on inspection of fig. 32, where P is the polariser, A the analyser, consisting of an achromatised

* In this section of the article 'Light' I am indebted to Dr. Armstrong, F.R.S., for many valuable additions and suggestions. H. W.

† In the description at p. 674, vol. III., it is stated (line 18 from top) that the incident light is polarised by the prism *n* the prism *c* is really the polariser.

calcspar prism, C the quartz-plate, and N the Nicol, which together constitute the regulator; the prism N is fitted in a milled collar B.

The scale of this instrument is constructed so that the space between 0 and 100 exactly represents the distance through which the quartz-wedges must be moved in

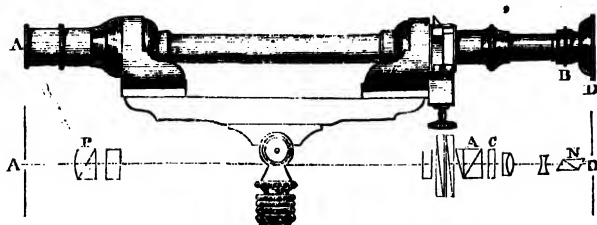


FIG. 32.

order to compensate the deviation produced by a plate of quartz 1 mm. thick placed between the polariser and analyser at right angles to their common axis, in the position ordinarily occupied by the substance under examination. Clerget in 1849 stated that a column 200 mm. in length of an aqueous solution containing 16.471 grams cane-sugar in 100 c.c., was capable of producing the same deviation of the polarised ray as such a plate of right-handed quartz; Dubrunfaut subsequently pointed out that only 16.390 grams were necessary, and the amount was afterwards still further reduced to 16.350 grams by a commission consisting of Barreswil, Duboseq, Pouillet and Schlösing.* The directions now issued with the instrument specify this last-named amount as that which is to be used in verifying the scale; and if this weight of a substance containing cane-sugar unmixed with any other optically active body be dissolved in water to 100 c.c., and the extent to which the wedges must be displaced in order to compensate the effect produced by a column 200 mm. in length of the solution be determined, the scale-reading directly represents the percentage of cane-sugar in the substance under examination †; if any other weight, w , of the substance be taken, and the extent to which the wedges must be displaced be ascertained, then calling this δ , the percentage of cane-sugar is given by the proportion

$$x = \frac{16.35 \times \delta}{w}$$

Soleil-Ventzke, or Soleil-Ventzke-Scheibler Saccharimeter.—The Soleil-Ventzke instrument differs from the Soleil only in possessing a different scale. The Soleil-Ventzke-Scheibler saccharimeter has in addition certain mechanical improvements introduced by Scheibler; the regulator is placed in front of the polariser, and only one wedge of the quartz compensator is movable. The disposition of the optical parts is shown in fig. 33.

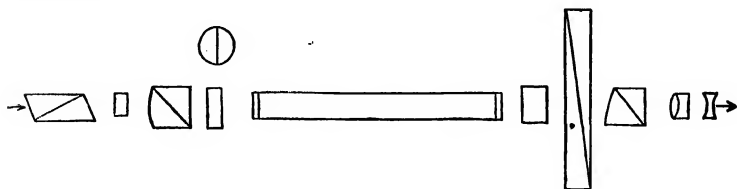


FIG. 33.

The Soleil-Ventzke scale is graduated by means of a solution of cane-sugar of the density 1.1 at 17.5°; such a solution is prepared by dissolving 26.048 grams of sugar to 100 c.c. The space through which the compensator is moved from the zero position in order to neutralise the effect of a column 200 mm. in length of the solution is divided into 100 equal divisions, so that if 24.048 grams of a substance containing cane-sugar as the only optically active constituent be dissolved to 100 c.c., and the

* Schmitz and Tollens' experiments indicate 16.302 grams as the proper amount (*comp. Landolt, Das optische Drehungsvermögen organischer Substanzen*: Brunswick, 1879, p. 206).

† This of course is true only on the supposition that the rotatory power of cane-sugar in solution is independent of the concentration, which it is not entirely (see pp. 1205, 1206).

solution be examined in a 200 mm. tube, the scale-reading will at once indicate the percentage of sugar.

The Soleil saccharimeter furnishes exact results only in the case of bodies which like cane-sugar and dextrose have the same or nearly the same rotatory dispersive power as quartz (see p. 1206), as the two halves of the field cannot be obtained of the same tint when substances which do not exhibit the same rotatory dispersive power as quartz—especially such as produce a considerable rotation of the plane of polarisation—are interposed between the polariser and analyser. Moreover many persons are either colour-blind or have a difficulty in judging of colours. These objections do not apply to the instruments now to be described.

Mitscherlich's Polarimeter.—The simplest form of polarimeter, often called by this name, consists of a polarising and analysing Nicol with the addition of a lens in front of the former to concentrate the light, and produce a circular field, and of a small telescope in front of the analyser (iii. 673). The analyser is attached to a vernier, capable of moving round a graduated circle. To set the instrument, and determine its zero-point, a ray of homogeneous yellow light from a sodium flame is passed along the axis, and the analyser is turned till the field of view exhibits the greatest darkness. This takes place in two positions 180 degrees apart, namely, when the principal sections of the polarising and analysing Nicol's prisms are at right angles to each other. If, however, the field of view be rather large, it does not become entirely dark, but is crossed by a vertical black band, which gradually becomes lighter towards the edges. This band should be exactly in the centre of the field when the index points to 0° . If now, the analyser having been brought to the zero-point, a tube filled with an optically active liquid be placed between the prisms, the field will appear more or less bright; and to measure the angle of rotation, the analyser must be turned to the right or to the left till the field or the black band in its centre again attains its greatest darkness.

If, however, the direction of the rotation be not previously known, the interpretation of the phenomena requires attention to the following considerations. Suppose

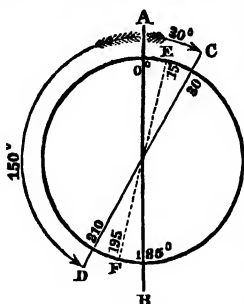


FIG. 34.

the plane of polarisation, originally in the position AB (fig. 34), to be turned by the action of the liquid into the position CD , making an angle of 30° with AB . The greatest darkness will then occur when the index points either to 30° or to 210° , indicating either a dextro-rotation of 30° or a levorotation of $360^\circ - 210^\circ = 150^\circ$. In nearly all cases the true rotation is in the direction of the smaller deflection. This, however, would not be the case if the angle of rotation were greater than 90° , which might occur if the rotatory power of the liquid were very great, or the tube more than 2 decimeters long. In such cases the question may be decided by using a tube of only half the original length, or diluting the solution to half its original strength. The rotation will thereby be reduced to half its original amount, and its direction will be easily recognised. If, for example, the field

becomes dark when the analyser is at 15° or 195° , the decrease takes place in the direction of dextro-rotation, whereas the angle measured to the left increases from 150° to 160° , which is inconsistent with the conditions of the experiment.

Wild's Polaristrobometer.—This instrument, invented by Wild in 1864 (*Ueber ein neues Polaristrobometer*, Bern, 1865), gives indications much more exact than those of Mitscherlich's apparatus. The essential feature of it is that between the polariser and analyser, the former of which is movable, there is inserted a Savart's polariscope, whereby a number of black interference bands are produced, which disappear in certain positions of the polariser. These positions, which can be sharply distinguished, afford the means of setting the instrument. The light used is that of the sodium flame screened by a plate of potassium bichromate.

The construction of the instrument is shown in figs. 35 and 36, the identical parts being indicated by small letters in the former, by capitals in the latter. The polarising and analysing arrangements are fixed at the ends of a brass frame Y , moving horizontally and vertically on the stand X . The light entering at a into the tube b passes first through the round diaphragm c (10 mm. in diameter), and then through the Nicol d . The mounting of these pieces is firmly attached to the circular disc e , and may be turned therewith round the axis. The polarised rays pass through the active liquid in the tube f , and lastly enter the fixed eye-piece. This part of the instrument, called the *polariscope*, contains: first, the part which yields the sensitive interference phenomena, namely, two plates of calcspar each 3 mm. thick, cut at an angle of 45°

to the optic axis, and cemented together in such a manner that their principal sections are at right angles to one another. Next follow two lenses *h* and *i* (of 120 mm. focal length), forming a telescope which magnifies about 5 times, with an arrangement for altering the distance of the latter. Between these, and in the focus of the object-lens *h*, is a circular diaphragm *k*, of about 4 mm. aperture, and provided with cross-wires

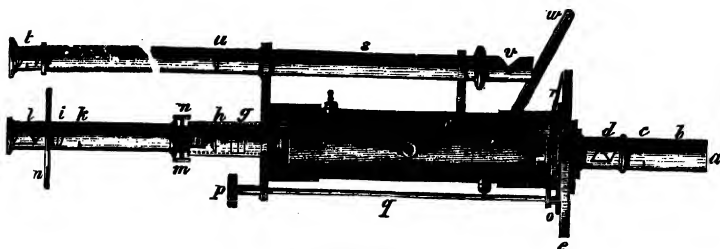


FIG. 35.

in the form of a cross. Lastly comes the Nicol's prism *l*, mounted with its principal section horizontal, and therefore inclined at 45° to the crossed principal sections of the double plate *k*. To keep the parts *g* and *l* in the same position, the movable part of the eye-piece containing the Nicol and the lens *i* is furnished with a guiding pin. The

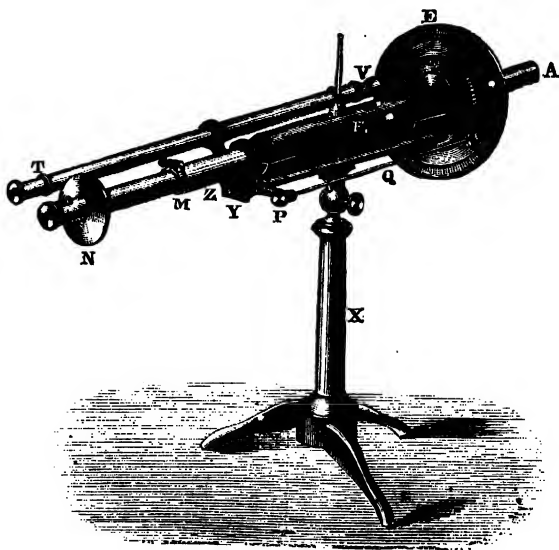


FIG. 36.

entire polariscope slides within a tube *Z*, fixed on the horizontal frame *Y*, and can be rotated therein through a small angle, for which purpose the tube *z* is provided with a guiding slit, and two clamping screws *m m*. A circular screen is fixed at *n* to protect the eye of the observer from extraneous light.

To enable the polarising Nicol to be rotated, its mounting, together with the circular disc attached to it, moves within a ring, fixed to the frame *Y*. The disc carries, on the side next the observer, a toothed wheel, and in this works the pinion *e*, which can be moved by the button *p* at the end of the rod *q*. The disc is graduated nearer its circumference, and in front of the graduation is fixed a vernier, or the simple index *r*. The graduation is read off by the telescope *s*, at the end *v* of which is an obliquely placed metallic mirror, with circular aperture, which reflects to the vernier the light of a small gas-flame placed on a movable arm. The instrument is usually made for

holding tubes up to 220 mm. in length. If it is to be used for scientific purposes, the disc must be graduated all round; for use in saccharimetry, a graduation extending only over one or two quadrants may be sufficient.

To set the instrument, the zero-points must first be determined by placing an empty tube in position and drawing out the eye-piece of the polariscope till the X-formed cross-lines are distinctly seen. If the polariser be then turned round by means of the button *p* (fig. 35), a position will be found in which the field of view will be traversed by a number of black parallel bands or fringes (fig. 37*a*). On continuing to turn, these fringes gradually become paler, and a point is at length reached at which a portion of the field appears bright and free from bands. By a slight backward and forward movement of the button, this bright portion may be brought into the middle of the field, and the remains of the fringes will still be visible at equal distances right and left of the cross-lines (fig. 37*b*). This position serves as the starting point for reading off the graduation. On turning the Nicol further round, the fringes first become stronger up to a certain maximum, then fainter till they disappear, and in a complete revolution of the disc this appearance may be observed four times, at intervals of 90° . In each of these positions the residual fringes usually assume a distinct form, which must be impressed on the memory (*comp.* Landolt, *op. cit.* p. 106).

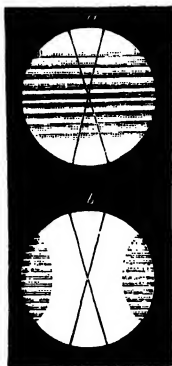


FIG. 37.

The disappearance of the fringes corresponds with those positions of the movable Nicol at which its principal section is either parallel or perpendicular to that of the first calcite plate of the polariscope, and, on the other hand, the greatest depth of the fringes takes place when these planes are inclined to one another at an angle of 45° . The optical parts of the instrument are adjusted by the maker in such a manner that the zero-points may fall nearly on the divisions 0° , 90° , 180° , and 270° ; they may, however, be shifted a little by means of the screws *m m*.

The movable Nicol having been brought to one of the four zero-points, the replacement of the empty tube by a tube filled with an active liquid, by which the plane of polarisation is turned through a certain angle, causes the interference-bands to reappear; and in order to bring the plane of polarisation back to parallelism or perpendicularity with that of the first plate of calcite, the Nicol must be turned round the opposite way, *i.e.* to the left or right accordingly as the active substance is dextro- or lævogyrate: the fringes will then reappear.

If the direction of rotation of the active liquid is not previously known, it is best ascertained by filling the tube with a dilute solution of the substance, so as to produce only a slight deviation, the direction of which, right or left, is easily distinguished. If, on the other hand, the deflections are of larger amount, doubts may arise as to

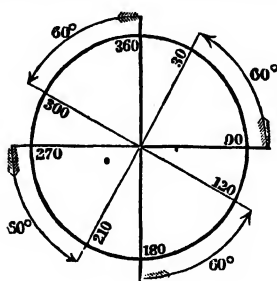


FIG. 38.

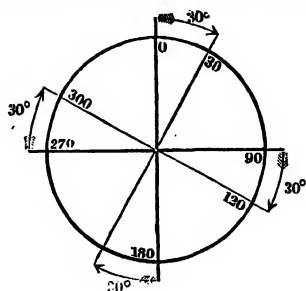


FIG. 39.

their direction, in the same manner as with Mitscherlich's apparatus. Suppose, for example, that the four zero-points are situated at

0° 90° 180° 270°

and that after insertion of the tube containing the active liquid, the fringes disappear at

30° 120° 210° 300°

then, as shown by figs. 38-41, the active liquid may be either dextrogyrate with an angle of 30° (fig. 39), or lævogyrate with an angle of 60° (fig. 38).

To decide the question, a second observation must be made either with a shorter tube or with a weaker solution. If, for example, the length of tube, or the concentration, in the second experiment, be only half that in the first, the angles of rotation will also be reduced to one-half their former magnitude. The fringes will therefore disappear at the positions

if the liquid is dextrogyrate (fig. 41), or at
 if it is lævogyrate (fig. 40).

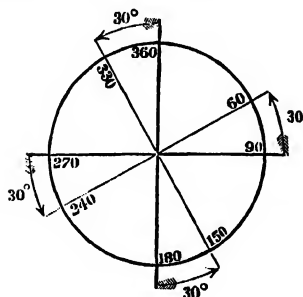


FIG. 40.

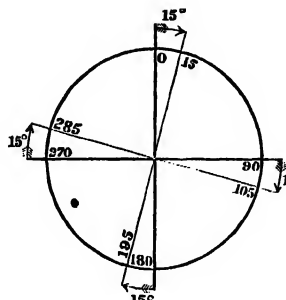


FIG. 41.

If, therefore, the observation with the shorter tube or weaker solution gives a number smaller than that obtained in the first experiment, the rotation is to the right; if, on the contrary, a larger number is obtained in the second experiment, the rotation is to the left.

In the examination of highly active liquids, it may happen that the angles of rotation exceed 90° , so that the readings fall in the following quadrants. To avoid errors in such cases, it is in like manner necessary to make observations with two tubes differing in length. Lævogyrate nicotine, for example, in a tube 100 mm. long, gave, in round numbers, the following results:—

	Quad. I	Quad. II	Quad. III	Quad. IV
Empty tube	90	180	270	360
Filled tube	18	108	198	288
Angle of Rotation	72	72	72	72

On repeating the observation with a tube 50 mm. long, the results were:—

	Quad. I	Quad. II	Quad. III	Quad. IV
Empty tube	90	180	270	360
Filled tube	9	99	189	279
Angle of Rotation	81	81	81	81

Instead, therefore, of the half-deflection expected in the latter case, a deflection was obtained even greater than that with the longer tube. If 50 mm. nicotine produce a deflection of 81° , 100 mm. should give 162° , and this result is, in reality, obtained when the zero-points in the second series of observations corresponding with this double length of tube are shifted one quadrant to the right. We have then:—

Empty tube	II 180	III 270	IV 360	I 90
Filled tube	I 18	II 108	III 198	IV + 72 (= 360-288)
Angle of Rotation	162	162	162	162

These relations may be made clearer by inspection of figs. 42 and 43, the former of which represents the rotation for a column 50 mm. long, the latter for 100 mm.

In all exact experiments it is necessary to carry out the observations in all the four quadrants. It will then be found that the observed angles of rotation differ from one another by somewhat considerable amounts, the differences arising from

defects in the construction of the Nicols, and from inexact mounting of the two calcite plates of the Savart's polariscope. These errors, however, may be made to disappear completely by taking the mean of the angles of rotation observed in the four quadrants.

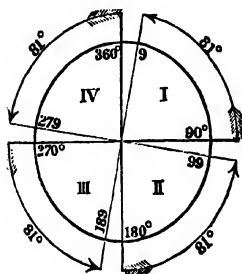


FIG. 42.

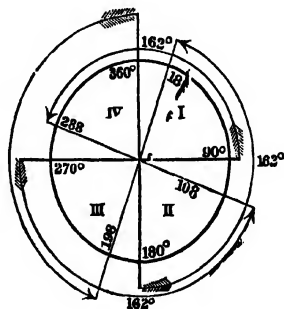


FIG. 43.

Half-shadow Polarimeters (Polarimètres à penombre).—In these instruments, invented by Jelett, Cornu, and Laurent, the circular field of view is divided into two equal parts which, within certain positions of the analyser, are unequally darkened, but in one particular position exhibit a faint and equal degree of shading. This point, which may be very exactly observed, serves for setting the instrument. The light used is that of the sodium-flame.

The penumbral apparatus most in use, especially for saccharimetry, is that of Laurent (*Dingl. pol. J.* ccxxiii. 608) represented in section in fig. 44, where a is a

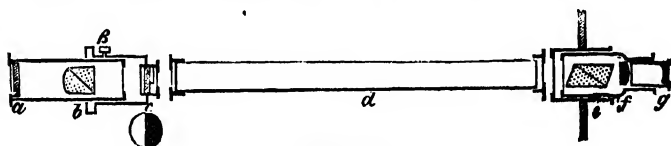


FIG. 44.

thin plate of potassium dichromate, serving to free the yellow light from admixed green, blue, and violet light; b the polarising prism; c a diaphragm carrying a glass plate to which a thin plate of quartz, cut parallel to the axis, is affixed so as to cover exactly one half of the field; d the tube containing the active liquid; e the analysing Nicol's prism; and fg a Galilean telescope of low power. The analyser is moveable, the extent to which it is moved being read off on a divided circle. The observation is made with a sodium-flame.

The quartz plate is of such thickness that, in their passage through it, the yellow rays polarised parallel and perpendicular to its axis suffer a retardation of exactly

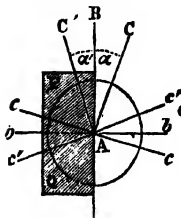


FIG. 45.



FIG. 46.

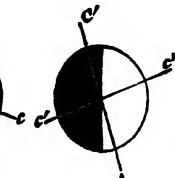


FIG. 47.

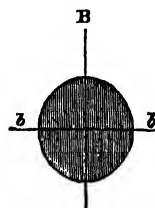


FIG. 48.

half a wave-length. When the polariser is set so that the entering rays are polarised in a plane AB parallel to the axis of the quartz plate PQ , fig. 45, both halves of the field are of the same relative intensity, whatever the position of the analyser; but if

the quartz plate be inclined at an angle α to A B, the rays passing through the plate are deflected to an equal extent α' , in the opposite direction, so that whenever the plane of polarisation is in the direction A C in the uncovered half of the field, it is in the direction A C' in the covered half. On turning the analyser, the rays polarised parallel to either A C or A C' are extinguished according as the plane of polarisation of the analyser comes into the position cc or $c'd'$ (figs. 46, 47); so that while one half of the field appears perfectly dark, the luminous intensity of the other half is only partially diminished; when it attains the position bb (fig. 48), the intensity is diminished to a. equal extent in either half, and the whole field is uniform in tone; a very slight movement in either direction, however, then causes a perceptible difference in the intensity of the two halves.

When the polariser and analyser are set with their principal sections at right angles, the field of view appears darker the smaller the angle α at which the plane of polarisation of the polariser is inclined to the axis of the quartz plate. The instrument is provided with an adjustment which permits of a slight alteration of the position of the polariser relatively to the quartz plate; it is the more sensitive, however, the less the polariser is moved from the normal position.

Jelett-Cornu Shadow Polariscopes.—This consists of an ordinary Nicol's prism, as analyser, and a peculiarly constructed Nicol, devised by Jelett, as polariser; the analyser is movable, and is associated with a divided circle. Yellow monochromatic light is employed in making the observation, a plate of bichromate being placed before the polariser. The polariser is constructed by cutting through an ordinary Nicol across the shorter diagonal and grinding down the two cut surfaces 2.5° ; the two halves are then cemented together again, and thus form a double Nicol having two principal sections inclined at 5° . The field presents precisely the same appearance as that of the Laurent instrument; on turning the analyser until its principal section is at right angles to one of the principal sections of the polariser, the corresponding half of the field becomes perfectly dark; a rotation of 5° renders the other half dark instead, but at an intermediate position of the analyser, the two halves of the field, although perfectly dark, are of equal intensity. Both with this and the Laurent instrument it is necessary to use a light of considerable intensity, and it is of considerable advantage to concentrate the light by means of a lens interposed between the flame and the polariser.

Usually only one half the circle of the Wild, Laurent, and Jelett-Cornu polariscopes is divided into degrees, the other half bearing a sugar scale; but different scales are adopted by the various makers. Thus the sugar scale of the Jelett-Cornu instrument manufactured by Duboscq of Paris is similar to the Soleil saccharimeter scale, an arc of $21^\circ 40'$ being divided into 100 equal divisions, and each division indicating 1 per cent. of cane-sugar when the solution examined is prepared by dissolving 16.35 grams of substance to 100 c.c. The Laurent polariscopes made by Schmidt and Haensch of Berlin is provided with the Ventzke scale, each division indicating 1 per cent. of sugar when 26.048 grams of substance is taken. The Wild polaristrometer, manufactured by Hermann and Pfister of Bern, has yet a different scale, based on the observation that a 200 mm. column of a solution containing 40 grams cane sugar in 100 c.c. has a rotatory power of 53.134° ; an arc of this extent is divided into 400 equal divisions, so that if 20 grams of substance be dissolved to 200 c.c. and the solution examined in a 200 mm. tube, the number of divisions of the scale through which the index is moved multiplied by 2 expresses the percentage of sugar present.

If it be desired to convert the scale-readings of either form of the Soleil saccharimeter into actual degrees, it is simply necessary to bear in mind that, according to Broch, a plate of quartz 1 mm. in thickness rotates the plane of polarisation of light of the refrangibility of the D lines 21.67° , and the medium yellow rays 24.5° ; therefore:

$$\begin{aligned} 1 \text{ division Soleil-Duboscq (j)} &= 0.2167^\circ \alpha_D \\ 1 \text{ " " " " } &= 0.245^\circ \alpha_j \end{aligned}$$

The divisions of the Soleil-Ventzke scale are $\frac{26.048}{16.35} = 1.593$ times as large as those of the Soleil-Duboscq scale.

As already pointed out, each division of the Soleil-Duboscq or Soleil-Ventzke scale represents the same amount of sugar, only if the rotatory power of cane sugar in solution be independent of the concentration; but the experiments of Schmitz and Tollens have shown that this is not quite the case. The following table shows the extent to which the scale readings of the Soleil-Duboscq instrument require correction (Landolt, *op. cit.* p. 167):

Scale reading	Corrected scale reading	Difference	Grams of sugar in 100 c.c. of solution		
			Uncorrected	Corrected	Difference
100	100.00	—	16.350	16.350	—
90	89.98	.02	14.715	14.712	.003
80	79.97	.03	13.080	13.075	.005
70	69.96	.04	11.445	11.438	.007
60	59.95	.05	9.810	9.802	.008
50	49.95	.05	8.175	8.167	.008
40	39.95	.05	6.540	6.532	.008
30	29.96	.04	4.905	4.898	.007
20	19.97	.03	3.270	3.265	.005
10	9.98	.02	1.635	1.632	.003

The correction is slightly higher in the case of the Soleil-Ventzke instrument, although for solutions containing less than 16 and above 85 per cent. it is so small that it may be neglected. Schmitz has calculated a table giving the correction for each scale division between 0 and 100 (see Landolt, *op. cit.* p. 156).

Determination of the Angle of Rotation for different Rays by Broch's (Fizeau and Foucault's) method.—The instruments above described allow only of the determination of the rotatory power for the medium yellow rays or for light of the refrangibility of the D lines; the rotatory power for rays of other wave-lengths may, however, be determined by the method indicated by Broch, and simultaneously by Fizeau and Foucault in 1846, by combining a spectroscope with an ordinary polariscope of two Nicol's prisms. By means of a heliostat, a horizontal beam of sunlight is reflected into a darkened room and allowed to fall on the polariser, and a spectroscope, the eyepiece of the observing telescope of which is provided with cross-wires, is placed in front of the analyser. In the first instance, the polariser and analyser are set with their principal sections at right angles, so that the light is completely extinguished. On introducing the substance, the rotatory power of which is to be measured, between the Nicols—since the planes of polarisation of the various components of the white light are deflected to a different extent in their passage through the active substance, and the colour whose plane of polarisation is perpendicular to that of the analyser is extinguished—the emergent light is coloured, and the spectrum seen on looking through the spectroscope contains, in addition to the ordinary Fraunhofer lines, a black band which shifts its position as the analyser is rotated. The observation consists in adjusting the cross-wires so as to coincide with one of the Fraunhofer lines, and then rotating the analyser until the centre of the black band is in the position previously occupied by the Fraunhofer line. The angle through which the analyser has been moved is then read off on the divided circle to which it is attached; and this reading represents the angular deviation of light of the wave-length of the particular line. V. von Lang has employed this method (*Pogg. Ann.* clvi. 422) in determining the rotatory power of quartz for light of the refrangibility of the red lithium line, the yellow sodium line, and the green thallium line, using artificial light, and this modified form of the method is probably of wide application. First a Bunsen flame is placed in front of the polariser, and a salt is heated in it capable of yielding a spectrum containing the line of the desired wave-length (a Geissler tube containing hydrogen may also be employed); the cross-wires of the spectroscope having been adjusted to this line, the Bunsen is replaced by an Argand burner, and the analyser rotated until the black band, which is seen on a background of continuous spectrum, is coincident with the cross-wires. In determining the rotatory power for rays near the limits of the visible spectrum, it is necessary to employ the lime light as the source of the continuous spectrum, as the light from an Argand burner is not rich enough in rays of extreme refrangibility to illuminate sufficiently the region on either side of the dark band. The chief objection to this method arises from the difficulty of determining exactly the position of the centre of the band, because of the gradual manner in which it shades off on either side: hence also consecutive readings are liable to differ to a greater extent than is usual with the instruments ordinarily employed. The method furnishes the most accurate results with substances of medium rotatory power (comp. Wiedemann, *Pogg. Ann.* (1851), lxxxii. 215).

Accuracy of various forms of Polariscope.—According to Landolt (*op. cit.* p. 117), equally accurate results may be obtained with either Wild's or Laurent's or even Mitscherlich's instrument, the numbers furnished by the three differing

at most in the second and very often only in the third place of decimals. The results of two practised observers with the same instrument agree to a few hundredths of a degree.

Influence of Wave-length on the Angle of Rotation.—The rotation of the plane of polarisation produced by the passage of a ray through a given thickness of an optically active substance, increases in nearly all cases as the wave-length diminishes, being least for red and greatest for violet light. Biot inferred, from observations on quartz, that the angle of rotation is inversely proportional to the square of the wave-length (iii. 72). Recent observations have shown, however, that this law is not exact, and Boltzmann (*Pogg. Ann. Jubelbd.* 1828, 28) has shown that the formula

$$\alpha = \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

where A and B are constants to be determined by experiment, agrees very closely with the results of observation. From measurements by Stefan (*Pogg. Ann.* cxxii. 631) and v. Lang (*ibid.* clvi. 422), on the rotatory power of quartz for the several lines of the spectrum, Boltzmann has calculated the formula

$$\alpha = \frac{7.07018}{10^6 \lambda^2} + \frac{0.14983}{10^{12} \lambda^4}$$

which differs from the results of observation only by hundredths of a degree.

On comparing the angles of rotation for light of the refrangibility of several of the chief spectral lines in different bodies, it is found that, besides the absolute differences of value for the same ray in different bodies, there are also differences in the relative values: in other words, the rotatory dispersive power is different for different bodies. Thus taking the results of measurements of the rotatory powers of a number of substances specified in the following table:—

		B	C	D	E	F	G
Quartz . . .	1mm.	15.55°	17.22°	21.67°	27.46°	32.69	42.37°
Cane-sugar . . .	[a]	47.56	52.70	66.41	84.56	101.18	131.96
Cholic acid . . .	[a]	28.2	30.1	33.9	44.7	52.7	67.7
Cholesterin . . .	[a]	20.63	25.54	31.59	39.91	48.65	62.37
French turpentine oil .	α100 mm.	21.5	23.4	29.3	36.8	43.6	55.9
Lemon oil . . .	α110 mm.	34.0	37.9	48.5	63.3	77.5	106.0

and calculating the ratios of the rotation of rays of the refrangibility of the lines C D E F G to that for the line B, the results exhibited in the following table are obtained:—

	B	C	D	E	F	G
Quartz	1	1.11	1.39	1.77	2.10	2.72
Cane-sugar	1	1.11	1.40	1.78	2.13	2.77
Cholic acid	1	1.07	1.20	1.59	1.87	2.40
Cholesterin	1	1.24	1.53	1.93	2.36	3.02
French turpentine oil .	1	1.09	1.36	1.71	2.03	2.60
Lemon oil	1	1.11	1.43	1.86	2.28	3.12

Hoppo-Seyler has determined the specific rotatory power of dextroglucose for light of the refrangibility of the C, D, E, and F lines with the following results:—

[α] _C	[α] _D	[α] _E	[α] _F
42.45	53.45	67.9	81.3

and dividing these by the rotatory power of 1 mm. of quartz, the following ratios are obtained:—

2.46	2.47	2.47	2.49
------	------	------	------

These numbers show that quartz, cane-sugar, and dextroglucose have equal rotatory dispersive powers, whereas in other bodies the rotatory dispersion is either greater or less than in quartz. This circumstance is of importance with regard to the use of the Soleil saccharimeter (iii. 674), the construction of which is based on the assumption of the equality of dispersion of the substance under examination with that of quartz; and as this appears to be the case only with cane-sugar and dextroglucose, it follows that the rotatory powers of other bodies cannot be exactly determined with this form of instrument.

Anomalous Rotatory Dispersion.—Tartaric acid in both its modifications offers a remarkable exception to the rule above stated that the deviation which a polarised ray undergoes in its passage through an optically active substance is greater the shorter its wave-length. This was first observed by Biot, but Arndtsen established

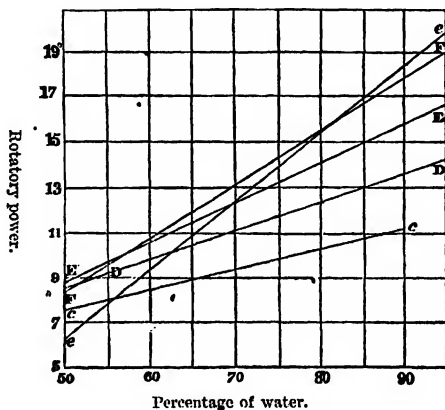
the law of the phenomenon (*Ann. Chim. Phys.* [3], liv. 415). The rotatory power of tartaric acid in aqueous solution varies greatly with the concentration, but in such a manner that it may be represented by the linear equation

$$[\alpha] = A + Bc,$$

where c is the percentage of water present. From experiments with solutions containing from 5 to 50 per cent. of the dextro-acid, Arndtsen has deduced the following values of A and B for light of the refrangibility of the lines C, D, E, b, F, e.

$$\begin{aligned} [\alpha]_C &= + 2.748^\circ + 9.446^\circ c \\ [\alpha]_D &= 1.950 + 13.030 c \\ [\alpha]_E &= .153 + 17.514 c \\ [\alpha]_b &= - .832 + 19.147 c \\ [\alpha]_F &= - 3.598 + 23.977 c \\ [\alpha]_e &= - 9.657 + 31.437 c \end{aligned}$$

The results are represented graphically in the following table:—



It will be noticed that solutions containing not less than about 85 per cent. of water exhibit a normal behaviour, exercising a maximum rotatory effect on the most refrangible rays, but that as the concentration increases, the point of maximum effect gradually passes to the other end of the spectrum, the most refrangible rays being the least rotated by a solution containing about 55 per cent. of the acid. Evidently the lines e e, F F, and E E, if prolonged, would cut the base line at a point between 0 and 50: in other words, rays of these refrangibilities would suffer lævorotation in their passage through highly concentrated solutions of dextrotartaric acid. The rotatory power of the acid itself may be calculated to be as follows:

$$[\alpha] = \begin{array}{cccccc} C & D & E & b & F & e \\ + 2.748^\circ & 1.950^\circ & .153^\circ & - .832^\circ & - 3.598^\circ & - 9.657^\circ. \end{array}$$

Solutions to which only a very small amount of boric acid has been added, or heated solutions, do not exhibit the above-described anomalous behaviour (Biot; Krecke).

Two optically active, chemically indifferent bodies of opposite rotatory power, having *different rotatory dispersive powers*, if mixed in certain proportions, would (as Biot has shown for a solution of dextrorotatory camphor in lævorotatory turpentine oil) exhibit phenomena similar to those manifested by tartaric acid solutions; hence the most probable explanation of the anomalous rotatory dispersive power of solutions of tartaric acid would appear to be that they contain, besides the acid, a compound of opposite rotatory power of the acid with water, in proportions varying according to the concentration and temperature of the solutions.

Influence of Temperature on Rotatory Power. According to Tuchschnid (*J. pr. Chem.* [2], ii. 235), the specific rotatory power of cane-sugar in aqueous solution is not affected by alterations of temperature; the same is true of the specific rotatory power of camphor in alcoholic solution (*ibid*), but the specific rotatory power of the majority of substances varies with the temperature, and most frequently diminishes as the temperature rises; lævulose is a notable example of this kind of alteration.

Gernez has investigated the alteration in specific rotatory power with rise of temperature of a number of terpenes and of camphor, and has extended his observations to temperatures above their boiling points. The results obtained for French turpentine and camphor are exhibited in the following table (*Ann. scient. de l'Ecole norm. sup. i. 1*):—

Tempera'ure	Density referred to water d	Observed angular deviation α	Length of tube l	Sp. rot. power $[\alpha] = \frac{\alpha}{d \cdot l}$
<i>French Turpentine Oil.</i>				
Liquid	$\left\{ \begin{array}{l} 11^{\circ} \\ 98^{\circ} \\ 154^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} \cdot 8712 \\ \cdot 7996 \\ \cdot 7505 \end{array} \right.$	$\left\{ \begin{array}{l} 15\cdot 97^{\circ} \\ 14\cdot 47^{\circ} \\ 13\cdot 50^{\circ} \end{array} \right.$	$\left\{ \begin{array}{l} \cdot 5018 \\ \cdot 50215 \\ \cdot 50237 \end{array} \right.$
Vapour	168°	$\cdot 003987$	$5\cdot 76^{\circ}$	$40\cdot 61$
Vapour-density at $168^{\circ} = 4\cdot 981$. Theoretical density, $4\cdot 700$.				
<i>Camphor.</i>				
Fused	204°	$\cdot 812$	$31\cdot 46^{\circ}$	$\cdot 5509$
Vapour	220°	$\cdot 003843$	$10\cdot 98^{\circ}$	$40\cdot 63$
Vapour-density at $220^{\circ} = 5\cdot 369$. Theoretical density, $5\cdot 252$.				

These results are of especial importance, as they prove that the rotatory power of substances such as the terpenes is a property of the individual molecules, so that the optical differences between the various terpenes cannot be supposed to be due to their consisting of aggregates of different degrees of complexity.

Tartaric acid in aqueous solution exhibits a considerable increase of rotatory power with rise of temperature (Tuchschmid, *loc. cit.*; Krecke, *Arch. Neerland*, vii. 97). The following results of a series of observations with three different solutions have been published by Krecke:

Temperature	Percentage of tartaric acid.		
	40	20	10
0°	$[\alpha]_D = 5\cdot 53^{\circ}$	$[\alpha]_D = 8\cdot 66^{\circ}$	$[\alpha]_D = 9\cdot 95^{\circ}$
10	7·49	9·96	10·94
20	8·32	11·57	12·25
30	9·62	12·49	13·93
40	11·03	13·65	15·68
50	12·27	15·01	17·11
60	12·63	16·18	18·31
70	13·38	17·16	19·42
80	14·27	18·40	20·72
90	15·01	19·99	22·22
100	17·66	21·48	23·79

According to Biot, whereas fused liquid tartaric acid has a considerable dextro-rotatory power, the solidified acid is feebly laevorotatory.

Influence of neutral solvents and of optically inactive substances on the rotatory power. Biot was originally led, by the investigation of the rotatory power of cane-sugar, to the conclusion that the rotatory power of a solution of an active substance in an inactive medium was directly proportional to the amount of active substance present. In 1838, however, he discovered the exceptional behaviour of tartaric acid, and in 1852 he showed that the specific rotatory power of oil of turpentine dissolved in alcohol increased, while that of camphor dissolved in alcohol or acetic acid diminished, on increased dilution; also that the specific rotatory power of camphor deduced from observations with an alcoholic solution did not agree with that deduced from observations with an equally concentrated acetic acid solution (*Ann. Chim. Phys.* [3], xxxvi. 257; comp. *ibid.* lix. 206). The modifying influence of

neutral solvents does not appear to have been generally recognised until Oudemans in 1872 (*Liebig's Annalen*, clxvi. 65) and Hesse in 1875 (*ibid.* clxxvi. 89, 189) again directed attention to the subject.

The results of Oudemans are given in the following table, in which p denotes the ratio of the weight of the dissolved substance to that of the solution; and $[\alpha]$ the specific rotatory power (see p. 1210). The numbers show that different substances are affected by the same solvent in very different degrees.

Substance	Solvent	p	$[\alpha]$
Cane-sugar	Water	0.056	+ 66.9°
" " " "	Alcohol, 50 per cent. . . .	0.050	+ 66.4
Light Oil of Cubebs	unmixed	—	— 40.8
" " " "	Alcohol	0.061	— 41.6
" " " "	Benzene	0.060	— 41.6
" " " "	Chloroform	0.075	— 41.7
Cinchonine	Alcohol	0.006 to 0.008	+ 228
" " " "	Chloroform	0.004 to 0.005	+ 212
Cinchonine Sulphate	Water	0.014	+ 169
" " " "	Alcohol	0.023	+ 191
" " " "	" " " "	0.055	+ 193
Cinchonine Nitrate	Water	0.020	+ 154
" " " "	Alcohol	0.022	+ 172
Cinchonine Hydrochloride . .	Water	0.016	+ 162
" " " "	" " " "	0.026	+ 168
" " " "	" " " "	0.031	+ 156
" " " "	Alcohol, 93 per cent. . . .	0.054	+ 175
Brucine	" " " "	0.054	— 35
" " " "	Chloroform	0.019	— 127
" " " "	" " " "	0.049	— 119
Podocarpic Acid	Alcohol	0.04	+ 136
" " " "	" " " "	0.09	+ 136
" " " "	Ether	0.04	+ 130
" " " "	" " " "	0.07	+ 130
Sodium Podocarpate	Water	0.046	+ 82
" " " "	" " " "	0.064	+ 79
" " " "	" " " "	0.138	+ 73
" " " "	Alcohol	0.09	+ 86
Phlorizin	" " " "	0.046	+ 52
" " " "	Wood-spirit	0.039	+ 52

Mixtures of two solvents may modify the specific rotatory power in a manner quite different from what might be expected from their action when separate. In an alcoholic solution of cinchonine, about half the alcohol may be replaced by chloroform without any considerable alteration of the rotatory power, whereas in a solution of cinchonine in chloroform the replacement of only $\frac{1}{300}$ of that solvent by alcohol produces a difference of 4° in the specific rotatory power. This power is at its maximum ($\alpha = 237.3^\circ$) when the solvent consists of a mixture of 10 per cent. alcohol and 90 chloroform. These facts show the great care which is necessary in experiments of this kind, to ensure the perfect purity of the solvents used. All the bodies examined by Oudemans exhibited the greatest rotatory power in those solvents in which they dissolved most abundantly.

Hesse's observations, extending to over 50 substances lead to precisely similar conclusions. For example, the following maximum and minimum values of $[\alpha]$ were found on examining solutions in various media of equal weights of the substances specified.

Elaborate observations on the influence of inactive solvents have also been made by Landolt (*Liebig's Annalen*, clxxxix. 241-337; *Deut. Chem. Ges. Ber.* ix. 901-914). This chemist has stated that a solution of tartaric acid in methylic alcohol is optically inactive (*ibid.* vi. 1078).

Tollens and Schmitz (*Deut. Chem. Ges. Ber.* x. 1403, 1414) have shown that the specific rotatory power of cane-sugar slightly increases, while, according to Tollens (*ibid.* ix. 1531), that of dextrose diminishes in a somewhat greater proportion with increased dilution.

	Maximum	Minimum	Difference
Tartaric Acid	+ 14.18°	+ 3.20°	10.98°
Quinic Acid	- 44.09	- 39.20	4.89
Santonine	- 176.50	- 171.53	4.97
Codeine	- 137.75	- 111.50	26.25
Laudanosine	- 105.00	- 56.00	49.00
Quinine	- 169.25	- 116.00	53.25
Cinchonidine	- 119.54	- 83.86	35.88
Cinchonine	+ 237.27	+ 226.48	10.79

Acids, alkalis, and mineral salts also in many cases greatly modify the rotatory power of active substances when added to their aqueous solutions. Thus mannite, which alone in an aqueous solution exercises a very slight levorotatory effect, manifests a considerably greater levorotatory power in presence of alkalis; acids have no influence, but it becomes dextrorotatory on the addition of borax, sodium chloride, or sodium sulphate. An aqueous solution of calcium dextrotartrate is dextrorotatory, but if this salt be dissolved in hydrochloric acid, a levorotatory solution is obtained. The rotatory power of tartaric acid is considerably increased by the addition of borax or boric acid, but diminished by the addition of hydrochloric or sulphuric acid. Many other similar cases of alteration in rotatory power have been observed (comp. Landolt, *op. cit.*)

Definition of Specific Rotatory Power. Apparent and Absolute Specific Rotatory Power. The specific rotatory power $[\alpha]$ of a substance for light of any particular refrangibility, according to Biot's definition, is the angular deviation imparted to the ray observed by a column of unit length and density, and is expressed by the formula

$$[\alpha] = \frac{\alpha}{l \cdot d},$$

where α is the observed angle, l the length of column—the decimeter being taken as the unit of length, and d the density of the substance; or, in other words, if the density be referred to water at 4°, the specific rotatory power is the angular deviation produced by a layer 1 decim. in length of a substance of which 1 gram occupies a volume of 1 c.c.

This formula, however, applies only to bodies which can be examined *per se*; if a solution of an active substance in an inactive solvent be employed for the determination, the specific rotatory power is deduced with the aid of the formula

$$[\alpha] = \frac{\alpha}{l \cdot e \cdot d},$$

where e is the amount of active substance in a unit of weight of solution, and d the density of the solution. If, as is frequently done, the amount of active substance in 100 parts by weight of the solution be determined, indicating this by p , the formula becomes

$$[\alpha] = \frac{100 \alpha}{l \cdot p \cdot d}.$$

But from the remarks made in the previous section it will be obvious that the specific rotatory power determined in this manner is not that of the substance itself, the specific rotatory power being in fact more or less modified by the association of the active substance with the inactive solvent, and the value obtained is applicable only to the solution of the particular strength and character observed. The value appertaining to the substance itself may be termed the *absolute* or *true specific rotatory power*, or simply the specific rotatory power; that appertaining to the substance in solution may in contradistinction be termed the *apparent specific rotatory power*. It may not be here out of place to insist on the fact that the former alone is a constant, and the only one which can be employed in the discussion of possible relations in rotatory power between optically active bodies.

In determining the *apparent* specific rotatory power, since $pd = c$, *i.e.* the concentration or number of grams of active substance in 100 c.c. of solution, the simpler formula

$$[\alpha] = \frac{100 \alpha}{l \cdot c}$$

is often employed.

The observed angular deviation is always indicated by the symbol α , the specific rotatory power by the symbol $[\alpha]$, the nature of the light for which the observation is made being represented by the index r, j, D , &c.; r applies to observations made with light which has passed through red glass, the use of which is now entirely abandoned; j applies to observations with the Soleil saccharimeter, where medium yellow light (*jaune moyen*) is employed; D indicates that light of the refrangibility of the D line is employed.

Tollens has suggested that the apparent specific rotatory power of a substance in a 10 per cent. solution should be termed the *conventional* specific rotatory power, and indicated by the symbol $[\alpha]_{10D}$; and that if so concentrated a solution cannot be obtained, a 5 or 2 per cent. solution should be employed, and the fact indicated by the use of the symbol $[\alpha]_{5D}$ or $[\alpha]_{2D}$ (*Deut. Chem. Ges. Ber.* x. 1412).

Kachler suggests (*Liebig's Annalen*, cxlvii. 88) that the rotatory power should be determined for solutions containing per litre a molecular proportion in grams of the respective active substances; inasmuch, however, as the rotatory power is not independent of the concentration, and the same solvent modifies the rotatory power of different bodies to very different extents, the advantage which such a proceeding offers of comparing the effects of equal numbers of molecules of the active substances is more apparent than real.

Determination of Absolute Specific Rotatory Power.—The mode of ascertaining the absolute specific rotatory power of bodies which cannot be examined *per se*, was first indicated by Biot (*Ann. Chim. Phys.* [3], xxviii. 236), but we are indebted to Landolt for a rigorous experimental examination of Biot's method (*Liebig's Annalen*, clxxxix. 241–337; *Deut. Chem. Ges. Ber.* ix. 901–914; *op. cit.* pp. 60–89). It consists in determining the apparent specific rotatory power for a series of solutions of various degrees of concentration, and thus ascertaining the influence of the solvent; the equation expressing the relation between the percentage of solvent q and the corresponding values of $[\alpha]$ is then sought, and this equation gives the value of $[\alpha]$, answering to $q=0$.

Landolt has determined the values of $[\alpha]_D$ for American and French turpentine oils, ethyl dextrotartrate, and nicotine, from observations with the pure substances as well as with a number of their solutions, with the following results:

Ethyl Dextrotartrate.

Direct observation	$[\alpha]_D =$	8.31°	Difference
From observation of mixtures with ethyl alcohol		8.27	+ .11
" " " methyl "		8.42	— .22
" " " water		8.09	

Dextrorotatory Oil of Turpentine.

Direct observation		14.15	+ .02
From observation of mixtures with ethyl alcohol		14.87	

Levorotatory Oil of Turpentine.

Direct observation		37.01	— .04
From observation of mixtures with alcohol		36.97	— .04
" " " benzene		36.97	— .12
" " " acetic acid		36.89	

Nicotine (levorotatory).

Direct observation		161.55	— .72
From observation of mixtures with alcohol		160.83	— .26
" " " water		161.29	

It will be observed that the values deduced from observations of the solutions are practically identical with those furnished by the pure substances.

The successful application of this method, however, depends on a variety of circumstances, and especially on the solubility of the substance and the manner in which the rotatory power is modified by the solvent. Landolt's experiments with the above-named liquids show that if the variation in rotatory power can be expressed with sufficient accuracy by a linear equation $[\alpha] = A + Bq$, extremely concordant results are obtained when the most concentrated solution examined contains no more than 50 per cent. of active substance; but that if it be necessary to employ an equation of the form

$$[\alpha] = A + Bq + Cq^2,$$

the rotatory power thus determined differs by more than a degree from that observed for the pure substance if the amount of extrapolation exceed 50 per cent., and in such a case accurate results can be obtained only if solutions containing at least 80 per cent. of active substance are examined. Thus in the case of French oil of turpentine, the value of A —the rotatory power of the pure substance—as deduced from various solutions, differs from the value 37.01° directly observed for the pure substance to the extent shown in the following table:

Solvent	Amount of extrapolation	A	Difference from true value 37.01
Alcohol	30 per cent.	37.20°	+ .19
	50 "	35.15	- 1.88
Benzene	35 "	37.26	+ .25
	63 "	35.42	- 1.59
Acetic Acid	22 "	36.65	- .36
	49 "	36.00	- 1.01

When, as in the case of nicotine dissolved in water, the rotatory power is very considerably modified by the solvent, and the curve representing the variation is hyperbolic, the absolute specific rotatory power can be calculated, with any approach to accuracy, only from observations with the most concentrated solutions, by an equation of the form $[\alpha] = A + Bq + Cq^2$; thus the value of $[\alpha]_D$ calculated from observations with three solutions containing respectively about 90, 78, and 66 per cent. of nicotine is 163.17, the true value being 161.55. The equation to the entire curve for nicotine and water is as follows:

$$[\alpha]_D = 115.019 - 1.70607q + \sqrt{2140.8 - 109.867q + 2.5572q^2}.$$

For pure nicotine ($q = 0$) this gives the value $[\alpha]_D = 161.29$, that directly observed being 161.55° . For $q = 100$, the value of $[\alpha]_D$ is 74.13 , so that the rotatory power of nicotine is diminished by more than one-half by great dilution.

In practice it is, therefore, necessary in the first place to select the solvent in which the substance to be examined most readily dissolves, and at least three solutions of different degrees of concentration are then examined. If, on representing the results graphically, making the percentages of solvent q the abscissæ and the corresponding values of $[\alpha]$ the ordinates, the three points of intersection are found to lie in the same straight line, the linear equation $[\alpha] = A + Bq$ capable of expressing the observations is calculated, and the constant A in this equation will be the specific rotatory power of the pure substance. If, however, the three points do not lie in the same straight line, further observations must be made in order to establish the character of the curve as completely as possible, and the equation to the curve is then sought. It is always desirable to examine solutions of the substance in a variety of media; if the values of A are fairly concordant, their mean is taken as the true value; but if they exhibit considerable discrepancies, the determination of the specific rotatory power in this manner must be abandoned. It appears to be useless to attempt the application of the method to substances of which solutions containing at least 50 per cent. of active substance cannot be prepared.

Landolt has determined the absolute specific rotatory power of camphor in this way (see p. 374), and Tollens has applied the method to dextroglucose and cane-sugar, the absolute specific rotatory power of the latter having also been determined by Schmitz (see pp. 1206, 1211). These are the only solid substances of which the absolute specific rotatory power is at present known.

Molecular Rotatory Power.—F. W. Krecke (*J. pr. Chem.* [2], v. 6) has made an extensive series of experiments on the effect of chemical combination on the molecular rotatory power (i.e. the product of the specific rotatory power* and the molecular weight) of organic bodies, and on the relations of molecular rotatory power in isomeric and allied bodies, from which he deduces the following conclusions: (1). When an optically active carbon-compound combines with an inactive body, or when it is modified by chemical reagents, the molecular rotatory power either remains unaltered, or is increased to a simple multiple of that of the primitive substance (see *Tartaric*

* In order to simplify the comparison of the numbers, Krecke, however, adopts the millimeter instead of the decimeter as the unit of length; the molecular rotatory power is therefore expressed by the formula,

$$[m] = \frac{[\alpha] \cdot m}{100},$$

where m is the molecular weight.

acid, p. 1219). (2). The molecular rotatory powers of isomeric bodies are multiples of one and the same number.

Krecke's conclusions are based, however, on the comparison of the apparent specific rotatory powers of the various substances, and little weight, therefore, can be attached to them. He points out that whereas the molecular rotatory powers of the various carbohydrates of the cane-sugar group are multiples of the mean factor 24.9, the molecular rotatory powers of the allied carbohydrates of the dextrose group are in like manner multiples of a mean factor which is about twice as great (48.5). It is noteworthy that the molecular rotatory powers of dextrose and cane-sugar calculated from Tollens's determination of the absolute specific rotatory powers of these bodies are approximately related in a somewhat similar manner, thus:

$$\begin{array}{l} \text{Dextrose } [\alpha]_D = 58.70 \\ \text{Cane-sugar } [\alpha]_D = 63.90 \end{array}$$

hence

$$\text{Dextrose } [m]_D = \frac{58.7 \times 180}{100} = 105.6 = 21.1 \times 5$$

$$\text{Cane-sugar } [m]_D = \frac{63.9 \times 342}{100} = 218.8 = 20.8 \times 10.$$

Theory of the Constitution of Optically Active Bodies. Of the three classes of crystalline circularly polarising bodies, nearly all those of the first class (vii. 745) occur in enantiomorphous hemihedral or tetartohedral forms; * and since bodies of this class are destitute of optical activity in the amorphous and liquid states, the property of circular polarisation must be ascribed to a peculiar arrangement of the molecules composing the crystals and not to any speciality of constitution of the molecules themselves. The constant correlation of the position of the hemihedral faces on the crystal and the direction in which the plane of polarisation is deflected by a substance, led Pasteur to infer that the molecules are arranged in such crystals in a right or left-hand spiral, a view which has been adopted by Rammeisberg and others, and has received much support from Solincke's recent observations (*Pogg. Ann. Erg. Bd. viii. 16*) that by arranging a number of thin plates of optically biaxial mica so that the principal section of each plate is equally inclined (by an angle of 45°, 60°, 90°, or 120°) to that of the previous plate, a combination may be obtained which behaves like an optically active crystal, rotating the plane of polarisation either to the right or to the left according to the direction in which the combination is arranged.

Pasteur also inferred (*Recherches sur la dissymétrie moléculaire des produits organiques naturels*. Leçons de Chimie professées en 1860, Paris, 1861), that a similar want of symmetry or opposition of structure characterises the molecules themselves of bodies which are optically active in the amorphous or liquid but not in the crystalline state, † and more recently this hypothesis has been further developed by Le Bel and van't Hoff, who have gone so far as to point out the special character in constitution of optically active bodies.

According to Le Bel (*Bull. Soc. Chim.* [2], xxii. 337), if in a compound of the form MA₄, where M is a simple or compound radicle associated with four replaceable monad atoms A, three of the four atoms A are replaced by three dissimilar monad radicles, simple or compound, the resulting molecule will be unsymmetrical, and as such will manifest the power of causing circular polarisation, provided (1) that in the original molecule the four groups A are not all disposed in a single plane of symmetry; and (2) that the group introduced in place of the third atom A is not of the same composition as the entire group with which it becomes associated; in this case, the compound will be inactive if the two equal groups exercise an opposite effect on polarised light. Thus in inactive tartaric acid it may be supposed that the two groups CH(OH).COOH are of opposite activity, and hence neutralise each other, whereas in the dextro- and lævo-rotatory acids they are identical and their effects are added. Le

* According to Groth (*Pogg. Ann.* cxxxvii. 433), we are entitled to assume that all such bodies are subject to enantiomorphous hemihedry or tetartohedry. Pasteur's researches (*Ann. Chim. Phys.* [3], xxxviii. 437) have, in fact, shown that many compounds of the second class, which under ordinary circumstances exhibit no signs of hemihedry, may be caused to furnish crystals with hemihedral faces by slightly modifying the conditions. Thus acid calcium malate, which invariably separates from a pure aqueous solution in holohedral forms derived from a right rhombic prism, at once exhibits hemihedral faces if crystallised from weak nitric acid.

† The bodies which, like tartaric acid, are optically active only in the amorphous condition or in solution, are all optically biaxial, and, as Landolt points out (*op. cit.*), there is no direction in which such crystals are single-refracting, so that the circular double refraction is masked by the much stronger ordinary double refraction. It is not therefore conclusively proved that they are inactive in the crystalline state.

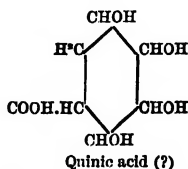
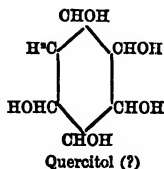
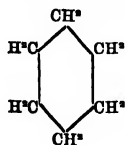
Bel points out that the constitution of the saturated compounds of the fatty series which are optically active, is such that in all cases the conditions of his hypothesis are satisfied.

The same idea has been more fully worked out and applied to numerous examples by van't Hoff in connection with his hypothesis of the orientation of atoms in space (see the article *ISOMERISM* in this volume, p. 1136).

According to this hypothesis, a body of the type CR^4 may be represented by a tetrahedron having the four radicles R , simple or compound, situated at the four summits and the carbon-atom in the middle; and if these four radicles are all different, they will, in consequence of unequal attraction, be situated at different distances from the carbon-atom, so that the compound $CR_1R_2R_3R_4$ will form an irregular tetrahedron having no planes of symmetry and capable of exhibiting enantiomorphous forms. Moreover, two tetrahedrons thus related exhibit, in relation to an axis drawn parallel to the corresponding edges, a screw-shaped grouping of the four summits, turning to the right in one form and to the left in the other. A carbon-atom thus united with four different radicles—called by van't Hoff 'asymmetric'—may therefore give rise to optical activity, and to the production of two modifications possessing equal and opposite rotatory power. A comparison of the formulæ of those optically active compounds derived from the paraffins, whose constitution is well established, shows that they all contain one or more asymmetric carbon-atoms, as will be evident from the examples given in the following table in which the asymmetric carbon-atoms are denoted by italic C 's:

C^3 group.	
Lactic acid	$CH^3-CH(OH)-COOH$
C^4 group.	
Malic acid	$COOH-CH^2-CH(OH)-COOH$
Malamide	$CONH^2-CH^2-CH(OH)-COOH$
Aspartic acid	$COOH-CH^2-CH(NH^2)-COOH$
Asparagine	$CONH^2-CH^2-CH(NH^2)-COOH$
Tartaric acid	$COOH-CH(OH)-CH(OH)-COOH$
Tartramide	$CONH^2-CH(OH)-CH(OH)-CONH^2$
C^5 group	
Secondary Butyl carbinol	$CH^3-CH^2-CH(CH^3)-CH^2OH$
Methylethylacetic acid	$CH^3-CH^2-CH(CH^3)-COOH$
Hydroxyglutaric acid	$COOH-CH^2-CH^2-CH(OH)-COOH$
Glutamic acid	$COOH-CH^2-CH^2-CHNH^2-COOH$
C^6 group.	
Secondary Butylacetic acid	$CH^3-CH^2-CH(CH^3)-CH^2-COOH$
Mannitol	$CH^2OH-(CHOH)^4-CH^2OH$
Glucose	$CH^2OH-(CHOH)^4-COH$
Saccharic acid	$COOH-(CHOH)^4-COOH$
Phenylhydroxyacetic (mandelic) acid	$C^6H^5-CH(OH)-COOH$

Two other interesting examples may be quoted, viz. quercitol and quinic acid. These compounds are very probably derivatives of a closed-chain hydrocarbon of the formula C^6H^{12} , derived from benzene, and if they are thus represented, it will be obvious that the groups are unsymmetrically arranged relatively to a plane of symmetry containing two of the hydroxyl groups:



The carbohydrates of the cane-sugar group and those of the empirical formula $C^6H^{10}O_6$, which are all closely allied in constitution to the glucoses, but of greater molecular complexity, as well as the glucosides, are undoubtedly to be represented by formulæ containing asymmetric carbon-atoms; and it is highly probable that this will also be found to be the case when the rational formulæ of the terpenes, camphors, alkaloids, albuminoids, and other complex optically active bodies become known.

There is nothing to indicate whether the mere presence of an asymmetric carbon-

atom in a compound is sufficient to endue it with optical activity, or whether it is necessary that the radicles associated with the asymmetric carbon-atom should be of a particular character. Different radicles evidently exert very different effects; no more striking example of this can be found than that afforded by so-called tartar-emetic, $K(SbO)C^*H^4O_6$, as compared with the other metallic tartrates (see TARTARIC ACID, p. 1219).

A compound of unsymmetrical formula containing n asymmetric carbon-atoms may exist in (2^n) isomeric modifications (p. 1138). Thus a compound of the form $C(R_1R_2R_3)C(R_4R_5—R_6)$ may exist in the four modifications indicated by the symbol

$$1) \begin{matrix} +A \\ +B \end{matrix} \quad 2) \begin{matrix} -A \\ +B \end{matrix} \quad 3) \begin{matrix} +A \\ -B \end{matrix} \quad 4) \begin{matrix} -A \\ -B \end{matrix}$$

Representing the rotatory power of the group A by the symbol $+A$ or $-A$, and that of the group B by $+B$ or $-B$, the rotatory power of each of these modifications will be as follows:

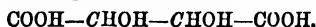
$$1) A + B \quad 2) -A + B \quad 3) A - B \quad 4) -A - B$$

Hence 1) and 4) and 2) and 3) will have equal but opposite rotatory powers. In a similar manner it may be shown that, always in the case of compounds of unsymmetrical formula, one half the isomerides are of equal but opposite rotatory power to the other half.

In the case of a compound of symmetrical formula containing two asymmetric carbon-atoms, three modifications are possible (p. 1138), the rotatory powers of which are as follows:

$$1) A + A = 2A \quad 2) A - A = 0 \quad 3) -A - A = 2(-A)$$

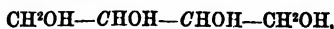
Two only of the three modifications of such a compound will therefore manifest optical activity, the third being inactive owing to what may conveniently be termed 'internal compensation;' and of this we have a most striking example in the three tartaric acids—dextro-, lævo-, and mesotartaric acid—which may be regarded as the three possible modifications of the compound of the formula



Racemic acid, if a definite compound, has at least double the molecular weight of tartaric acid. Berthelot and Jungfleisch's experiments (*Ann. Chim. Phys.* [5], iv. 147) render it probable that mere dissolution in water decomposes it into dextro- and lævotartaric acid. But whatever may be its nature, its inactivity is readily accounted for, since it consists of equal amounts of the two acids of equal but opposite activity. The inactivity of bodies which, like racemic acid, are readily formed by the mere admixture of two active substances, or which are resolved into inactive substances by similar—and almost by mechanical—means, may conveniently be said to arise from 'external compensation.'

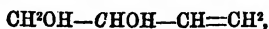
A large number of bodies are represented by formulæ indicating that they contain asymmetric carbon-atoms, but, nevertheless, they appear to be destitute of optical activity. From the preceding remarks it will be obvious that this may be the result of either 'internal' or 'external' compensation. Moreover many substances have been not at all, or but very imperfectly, examined with regard to their power of deflecting polarised rays, and their rotatory power may be so slight, or so difficult to observe on account of sparing solubility, that it has hitherto been overlooked.

Both Le Bel and van't Hoff have pointed out that, if a body which does not contain an asymmetric carbon-atom is converted, either by substitution or addition, into a compound containing one or more asymmetric carbon-atoms, it is to be expected that isomerides of equal and opposite rotatory power will be produced in equal quantities; and, as a matter of fact, racemic and mesotartaric acids have been produced artificially in a number of ways, but neither of the active modifications has ever been obtained by synthetical means.* On the other hand, according to van't Hoff, there is little hope of obtaining an optically active body from a compound of symmetrical formula which is inactive through internal compensation, by destroying its symmetrical character. For example, erythritol,

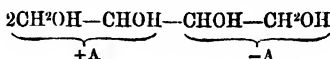


* Pasteur long ago showed that dextrotartaric acid was more readily destroyed than lævotartaric acid by certain minute organisms (*Penicillium glaucum*), a solution of racemic acid in which they were contained soon acquiring a levorotatory power. In a similar manner, according to Le Bel, the inactive alcohol obtained by distilling levorotatory fermentation amylic alcohol with sodium hydrate, yields dextrorotatory amylic alcohol when submitted to the action of *Penicillium*. As this article is passing through the press, Le Bel announces that it is possible also to obtain in this way an optically active (levorotatory) methylpropylcarbinol from the optically inactive methylpropylcarbinol prepared by reducing methylpropyl ketone (*Compt. rend.* lxxix. 312).

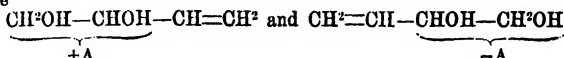
may be converted, by distillation with formic acid, into the glycol



and as this is a body of unsymmetrical formula, and contains an asymmetric carbon-atom, it should be optically active. But it is probable that while the group A of a certain number of erythritol molecules would be attacked, the group -A of an equal number of other molecules would undergo a similar change, and consequently the product would be an inactive mixture of bodies of equal but opposite rotatory power; thus



would give



Nevertheless there are a number of facts which appear to indicate that this may not always be the case. Thus mannitol, which probably is inactive in the pure state (see Müntz and Aubin, *Ann. Chim. Phys.* [5], x, 533), acquires a considerable dextro-rotatory power in presence of boric acid or borax, but is laevorotatory in presence of alkalis; and the dichlorhydrin, $\text{C}^2\text{H}^4\text{Cl}^2(\text{OH})^2$, obtained by heating it with hydrochloric acid is laevorotatory. Mannitol, however, is in many respects peculiar; if its inactivity is to be ascribed to 'internal compensation, a symmetrical alteration in its composition should not have the effect of converting it into an optically active body; but, as a matter of fact, mannite hexacetate, hexnitrate, and hexsulphate (*J. pr. Chem.* [2], xx, 13) manifest considerable dextrorotatory power. The examination of the mannitol regenerated from these compounds appears desirable.

Mannitol is not the only substance whose behaviour is in some respects difficult to harmonise with the hypothesis under discussion. Thus malic acid, which in a pure aqueous solution exhibits slight laevorotation, acquires an increased laevorotatory power on the addition of boric acid, but its solution in nitric acid is dextrorotatory; it cannot be supposed, in explanation of these phenomena, that, as in the case of mannite, the molecule consists of two symmetrical halves, +A and -A, and that the rotatory power of the one half is influenced by the boric acid and that of the other half by the nitric acid, since malic acid, $\text{COOH}-\text{CH}^2-\text{CHOH}-\text{COOH}$, contains only a single asymmetric carbon-atom. Again, asparagine and aspartic acid are dextrorotatory in acid solutions but laevorotatory in alkaline solutions. It is not easy to understand this behaviour on the hypothesis that they are derived from a single molecule of succinic acid and therefore contain only a single asymmetric carbon-atom, and the difficulty remains even if it be assumed that, as appears probable on other grounds, they are derived from a double molecule of succinic acid. Again, as already mentioned, the anomalous rotatory dispersive power of solutions of tartaric acid almost necessitates the assumption that the acid forms a compound with water opposite to itself in rotatory power; the formation of a body having a reversed rotatory power as compared with that of the parent substance from a compound like dextrotartaric acid which, according to van't Hoff's hypothesis has the constitution 2A, i.e. is composed of two similar dextrorotatory groups, is, however, not easy to understand.

One of the most remarkable facts in connection with optically active substances is the readiness with which many of them undergo alteration in rotatory power. Thus tartaric acid, as Pasteur and Jungfleisch have shown, may be converted by mere heating into mesotartaric and racemic acid, and in the same way mesotartaric acid may be transformed into racemic acid. According to Montgolfier, the hydrogenation of camphor gives rise to two distinct camphols of equal and opposite rotatory powers, both of which, however, give the same dextrocamphor on oxidation. In these cases the change produced in the direction of rotatory power persists as long as the compound is not destroyed, whereas in the cases above mentioned the change is dependent on the presence of another substance, and is in nowise perfect.

Whether facts such as these we have mentioned can be satisfactorily explained in accordance with the Le Bel-van't Hoff hypothesis has yet to be shown; the hypothesis appears, however, to be sufficiently in harmony with much of our knowledge to merit the most careful consideration.

Specific Rotatory Powers of various Bodies. *Quartz.*—The following table shows the angles of rotation (α) of the several spectral lines produced by a plate of quartz 1 mm. thick, according to the measurements of Stefan (*Pogg. Ann.* cxvii. 631), and for the lithium, sodium, and thallium lines by v. Lang (*ibid.* clvi. 422); also the corresponding wave-lengths λ , in ten-thousandths of a millimeter,

	B	C	D	E	F	G	H
λ	6871	6560	5888	5209	4860	4309	3967
α	15°55'	17°22'	21°67'	27°46'	32°69'	42°37'	50°98'

	Li	Na	Tl
λ	6703	5888	5346
α	16°43'	21°64'	25°59'

The values for the line D found by different observers are as follows:

Biot	20°98'	Wild	21°67'
Broch	21°67' ± 0.11	v. Lang (at 13°3')	21°64'
Stefan	21°67'	Soret a. Sarasin (at about 35°)	21°80'

v. Lang has shown that the rotatory power of quartz increases with rise of temperature, and that the relative alteration is the same for all colours: at 0° the values are—

	Li	Na	Th
α_0	16°402'	21°597'	26°533'

and for any temperature t —

$$\alpha_t = \alpha_0(1 + 0.000149 t).$$

According to later experiments by Sohncke (*Ann. Phys. Chem.* [2], iii. 516), the alteration caused by temperature is more correctly represented by the formula

$$\alpha_t = \alpha_0(1 + 0.0000999 t + 0.000000318 t^2).$$

Soret a. Sarasin (*Compt. rend.* lxxxii. 610) have measured the rotation produced by a plate of quartz for the ultra-violet rays as far as the line N_1 and have obtained values agreeing very nearly with Boltzmann's formula (p. 1207). The absolute values are somewhat smaller than those formerly obtained by Stefan (*Wien. Akad. Ber.* l. 88). The observations have been extended by Croullebois (*Compt. rend.* lxxxii. 666) as far as O, and subsequently by Soret a. Sarasin (*ibid.* lxxxiii. 818) as far as R.

Dithionates.—For the rotatory powers of the potassium, lead, strontium, and calcium salts, values have been obtained by E. Bichat (*Bull. Soc. Chim.* [2], xx. 436) agreeing very nearly with those determined by Papo (vii. 748). If the rotatory power of quartz be expressed by 100, those of the first three dithionates above mentioned will be 40, 24, and 8.

Cinnamene. Two specimens gave $[\alpha]_D = -3.1$ and -3.4 . For solid meta-cinnamene $[\alpha]_D = -2.2$ (Berthelot, *Compt. rend.* lxxxii. 441; lxxxv. 1191). Van't Hoff (*Deut. Chem. Ges. Ber.* ix. 5) maintains, however, that cinnamene has no rotatory power, and that the optical activity of that examined by Berthelot was due to an impurity.

Volatile Oils. These oils are for the most part mixtures of active and inactive constituents, so that their total rotatory power is the sum or difference of the rotatory powers of these constituents, modified by all the influences of solvents and other inactive substances above noticed. Moreover, the proportion of the several constituents often varies in the same oil, and chemical alterations may arise on keeping. All these circumstances influence the rotatory power, which is therefore by no means a trustworthy guide in distinguishing one volatile oil from another (Flückiger, *Arch. Pharm.* [3], x. 193).

Camphor. On the specific rotatory power of this substance in the solid state and in solution, see pp. 373, 374; of the Isomerides and Derivatives of Camphor and Camphol: Morgolfier (*Ann. Chim. Phys.* [5], xiv. 5–118; *Chem. Soc. J.* xxxiv. 891–903).

Camphor or Stearoptene of Matico-oil. The crystals of this substance belong to the trapezo-tetartohedral division of the hexagonal system. The rotation of a ray passing through a plate 1 mm. thick parallel to the axis is for red, yellow, and green light as follows:

Line	Li	Na	Tl
Rotation	1° 41'	2° 4'	2° 28'

No decided rotation was observed in a concentrated solution (Hintze, *Pogg. Ann.* clvii. 127).

Amyl-compounds. See vol. vii. p. 62.

Tartaric acid and Tartrates.—The influence of temperature on the rotatory power of these compounds has been examined by F. W. Krecke (*Archiv. néerl.* vii. 97), who has obtained the following results: (1). The specific rotatory power increases, in the case of tartaric acid, for all rays of the spectrum, but in very different degrees in solutions of different concentration. If the value at 0° = 1, that at 100° for the rays,

	C	D	E	b	F
is, in 50 per cent. Tartaric acid	2.3	2.5	2.7	3.1	3.4
„ 40 „	3.2	3.2	3.0	—	3.2

In the last case therefore it remains constant for the different colours; in the first it increases with the refrangibility. (2). In the 50 per cent. solution the line whose plane of polarisation is most turned round is situated, at 0° between D and E, at 25° close to E, and at 50° and higher temperatures it is advanced so far towards the violet, that in the experiments under consideration, it fell beyond the observed portion of the spectrum. The anomaly, peculiar to tartaric acid, of rotating the green rays more strongly than those either of greater or of lesser refrangibility, disappears therefore with rise of temperature and with progressive dilution. (3). The product of the specific rotatory power into the square of the wave-length which, according to Biot's law (iii. 672), should be constant, increases from the red to the violet. (4). The tartrates of potassium, sodium, and ammonium, Rochelle salt, and tartar emetic follow Biot's laws; their rotatory power increases or diminishes with the temperature in various degrees. The molecular rotatory power of the salts, with the exception of tartar emetic, is nearly three times as great as that of tartaric acid in the dilute stato. (6). In the salts examined, the product of the specific rotatory power into the square of the wave-length is a maximum for the green or for the yellow rays.

Landolt (*Deut. Chem. Ges. Ber.* vi. 1073) has also determined the molecular rotatory powers of a number of tartrates, and compared them with that of tartaric acid, for which he has calculated a new empirical formula representing the alteration of the specific rotatory power with the concentration. If $[\alpha]_D$ denote the specific rotatory power for the sodium-line D, the formula in question is

$$[\alpha]_D = 15.06 - 1.031 c,$$

in which c denotes the number of grams of tartaric acid in 100 c.c. of the solution. In the following table of results, $[M]_D$ denotes the molecular rotatory power of the salts, i.e. the product of the specific rotatory power and molecular weight. The solutions were prepared so as to contain 1 molecule of the salt to 100 molecules of water, i.e. in the case of pure tartaric acid, 7.69 grams to 100 c.c. The last column contains the quotients (Q), obtained by dividing $[M]_D$ by the rotatory power of the solution of tartaric acid just mentioned, viz. 21.08. P is the molecular weight.

Substance	P	$[\alpha]_D$	$[M]_D$	Q
$\text{LiHC}^4\text{H}^4\text{O}^6$	156	27.43	42.79	2.03
$(\text{NH}^4)\text{HC}^4\text{H}^4\text{O}^6$	167	25.65	42.84	2.03
$\text{NaHC}^4\text{H}^4\text{O}^6$	172	23.95	41.19	1.95
$\text{KHC}^4\text{H}^4\text{O}^6$	188.1	22.61	42.53	2.02
$\text{Li}^2\text{C}^4\text{H}^4\text{O}^6$	162	35.84	58.06	2.76
$(\text{NH}^4)^2\text{C}^4\text{H}^4\text{O}^6$	184	34.26	63.04	2.99
$\text{Na}^2\text{C}^4\text{H}^4\text{O}^6$	194	30.85	59.85	2.84
$\text{K}^2\text{C}^4\text{H}^4\text{O}^6$	226.2	28.48	64.42	3.06
$(\text{NH}^4)\text{NaC}^4\text{H}^4\text{O}^6$	189	32.65	61.71	2.93
$(\text{NH}^4)\text{KC}^4\text{H}^4\text{O}^6$	205.1	31.11	63.81	3.03
$\text{NaKC}^4\text{H}^4\text{O}^6$	210.1	29.67	62.34	2.96
$\text{MgC}^4\text{H}^4\text{O}^6$	172	35.86	61.68	2.93
$(\text{AsO})\text{HC}^4\text{H}^4\text{O}^6$	240	16.91	40.58	1.93
$(\text{AsO})\text{KC}^4\text{H}^4\text{O}^6$	278.1	21.13	58.76	2.79
$\text{K}(\text{SbO})\text{C}^4\text{H}^4\text{O}^6$	323	142.76	461.11	21.87
$\text{K}(\text{C}^2\text{H}^3)\text{C}^4\text{H}^4\text{O}^6$	216.1	29.91	64.64	3.07
$\text{Ba}^{\frac{1}{2}}(\text{C}^2\text{H}^3)\text{C}^4\text{H}^4\text{O}^6$	245.5	25.68	63.04	2.99

The numbers in the last column exhibit an approximation to the relation of simple multiples required by the law enunciated by Mulder and Kroeke, but as pointed out by Oudemans (*Ber.* vi. 1166, 1447) they are not exactly in accordance with it. It must be recollected, however, that the numbers in this table refer only to the *apparent* and not to the *absolute* specific rotatory power of the acid and its salts; properly speaking, only the absolute specific rotatory powers should be employed in such a discussion. The rotatory power of tartrates containing two different metals is equal to the arithmetical mean between the two corresponding simple salts, e.g.

	$[\alpha]_D$	$[M]_D$
$\text{K}^2\text{C}^4\text{H}^4\text{O}^6$	28.48	64.42
$\text{Na}^2\text{C}^4\text{H}^4\text{O}^6$	30.85	59.85
Mean	29.66	62.13
Found for $\text{KNaC}^4\text{H}^4\text{O}^6$	29.67	62.34
4 x 2		

Other salts, *e.g.* the compounds of potassium and sodium tartrate with the corresponding borates, exhibit, with increasing dilution, a rapid decrease of their originally strong specific rotation. In tartar-emetic the specific rotation is moderately constant and very large. For a solution of 7.892 grams in 100 c.c.:

$$[\alpha]_D = 143.01 \quad [M]_D = 464.93 \quad Q = 22 \text{ nearly.}$$

A different relation is exhibited by the tartaric ethers. In ethyl tartrate, $(C^2H^5)^2C^4H^4O^6$, the specific rotation in aqueous solution increases with progressive dilution, nearly in the same proportion as in aqueous tartaric acid, so that the two may be compared in equivalent degrees of concentration. In this manner the following numbers are obtained:

Ethyl Tartrate in 100 c.c. solution	$[\alpha]_D$	$[M]_D$	Eq. Concentration of Tartaric acid Solution	$[M]_D$ of Tartaric acid	$\frac{[M]_D \text{ ether}}{[M]_D \text{ acid}}$
10.489 grams	25.92	53.40	7.6376	21.09	2.53
5.2445 "	25.86	55.33	3.8188	21.84	2.53
2.6223 "	27.37	56.38	1.9094	22.22	2.54

Hence it appears that the molecular rotatory power of ethyl tartrate is about $2\frac{1}{2}$ times that of tartaric acid. It is possible, however, that this low value may be due to decomposition of the salt by water. A similar behaviour is exhibited by methyl tartrate.

The specific rotatory power of tartaric acid is much smaller in alcoholic than in aqueous solution. For a solution of 7.69 grams in 100 c.c. alcohol, $[\alpha]_D = 5.0$ and $[M]_D = 7.5$; the rotatory power is however increased by heating the solution in a sealed tube. Tartaric acid dissolved in methyl alcohol loses its rotatory power completely, but becomes active again when the solution is diluted with water.

Hesse (*Liebig's Annalen*, clxvi. 119) finds, for solutions of tartaric acid in which the value of c (the number of grams of substance in 100 c.c. of solution) is between 5 and 15, and temperature 15° , that $[\alpha]_D = 14.90 - 0.14 c$, and increases with the temperature by about a quarter of a degree to $7.5^\circ C$. Two experiments in which an aqueous solution of tartaric acid ($c = 15$) was mixed with 4 and 8 molecules (n) of hydrochloric acid gave $[\alpha]_D = 12.8 - 12 m$. For $c = 5$ in fuming hydrochloric acid, $[\alpha]_D = 4.2$. Neutral sodium tartrate, dissolved in water at 22.5° , gave, for values of c between 5 and 15, $[\alpha]_D = 27.85 - 0.17 c$. If, however, the solvent contains 1 or 2 mols. free soda to 5 grams of tartaric acid, the rotatory power is reduced to 26.36° or 25.6° respectively. The relations observed by Landolt (p. 1219) are, according to Hesse's observations, only approximately true.

Quinic acid, in aqueous solution ($c = 2$ to 10), gave $[\alpha]_D = 43.9^\circ$, and after two days 0.5° more. A solution in 80 v.p.c. alcohol ($c = 5$) gave $[\alpha]_D = -39.2^\circ$, the aqueous solution ($c = 2$), with 1 mol. Na_2O , gave $[\alpha]_D = -4.7^\circ$.

Sugars.—1. *Cane-sugar.* The specific rotatory power of this substance is $[\alpha]_D = 66.064^\circ$ according to L. Weiss (*Wien. Akad. Ber.* [2 Abth.], lxxix. 1); 67.18° according to De Luynes a. Girard (*Compt. rend.* lxxx. 1354). According to Hesse (*Liebig's Annalen*, clxxvi. 95) it is represented, for aqueous solutions, at the temperature 15° , and from $c = 0$ to $c = 10$ by the formula

$$[\alpha]_D = + 68.65^\circ - 0.828 c + 0.1154 c^2 + 0.005417 c^3.$$

For higher values of c , the rotatory power is nearly constant and equal to 66.5° . A rise of temperature of 10° makes no alteration in the value.

For solutions in 50 v. p. c. alcohol in which $c = 5$ $[\alpha]_D = 66.70^\circ$
 In water containing 1 mol. SO^2 " $c = 6$ $[\alpha]_D = 66.67$
 " " 1 mol. Na_2O " $c = 5$ $[\alpha]_D = 60.00$

Tollens (*Deut. Chem. Ges. Ber.* x. 1403) gives the following formulæ, in which p denotes the number of grams of sugar in 100 grams of solution: I. for $p = 0$ to 18, II. for $p = 18$ to 69, as the results of a series of most carefully conducted experiments:

$$\begin{aligned} \text{I. } [\alpha]_D &= 66.8102 - 0.015553 p - 0.000052462 p^2 \\ \text{II. } [\alpha]_D &= 66.386 + 0.015035 p - 0.0003986 p^2 \end{aligned}$$

According to Landolt's notation (p. 1211) in which $q = 100 - p$, these formulæ become:

$$\begin{aligned} \text{Ia. } [\alpha]_D &= 64.7303 + 0.026045 q - 0.000052462 q^2 \\ \text{IIa. } [\alpha]_D &= 63.9035 + 0.064685 q - 0.0003986 q^2 \end{aligned}$$

The weakest solution examined was that in which $p = 3.8$.

The term 'conventional specific rotation' is proposed by Tollens to denote, for most circularly polarising bodies, the apparent specific rotation produced in a 10 per cent. solution, this magnitude being represented for sodium light by the symbol $[\alpha]_D^{10}$. For cane-sugar the value of $[\alpha]_D^{10}$ is 66.65° . Fused anhydrous cane-sugar exhibits in the solid state a rotatory power = 46.91° ; in solution 48.00° , but since such a product strongly reduces in alkaline solution of a cupric salt, there is no doubt that the sugar is in part decomposed.

M. Schmitz (*Ber. x. 1414*), who has also very carefully determined the rotatory power of solutions of various degrees of concentration, finds for the temperature 20° , and for $p = 10$ to $p = 86^\circ$:

$$[\alpha]_D = 66.453 - 0.00123621 p - 0.000117037 p^2.$$

For weak solutions, $p = 2.5$ to 2.76 , the following is sufficiently exact:

$$[\alpha]_D = 66.541 - 0.00841532 p.$$

According to Tollens's experiments, the absolute specific rotatory power of cane-sugar is $[\alpha]_D = 63.9^\circ$; according to Schmitz's experiments it is $[\alpha]_D = 64.156^\circ$.

Experiments by H. Pollet (*Bull. Soc. Chim. [2], xxviii. 250*) on the influence of alkalis on the rotatory power of sugar have shown that this influence is much more powerful in concentrated than in dilute solutions. The following table shows how many grams of sugar in solutions of 17.3 and 5.4 per cent. respectively are rendered optically inactive by the addition of 1 gram of the substances mentioned in the first column:

	17.3 p. c. solution	5.4 p. c. solution
Sodium Carbonate	0.132	0.040
Sodium Phosphate (crystallised).	0.036	0.016
Caustic Soda (Na ² O)	0.450	0.14
Ammonia (NH ³)	0.085	0.073
Ammonium Carbamate (NH ² CO ²)	0.067	0.040
Potash (K ² O)	0.50	0.17
Potassium Carbonate	0.065	0.044
Lime	1.00	0.9
Baryta	0.43	0.19

2. *Milk-sugar*.—Ordinary milk-sugar, or α -Lactose, with 1 mol. H²O, gives for $p = 2$ and 3, respectively, the values $[\alpha]_D = 80.68$ and 79.70 . β -Lactose, which is formed from the preceding by long standing or by boiling, and is $\frac{2}{3}$ -times more soluble than α -lactose, gave between $p = 0$ and $p = 12$:

$$[\alpha]_D = + 54.54^\circ - 0.557 c + 0.05475 c^2 + 0.001774 c^3.$$

The rotatory powers of the two modifications are to one another in the ratio 3 : 2, which is the inverse of that of their solubilities. On addition of 1 mol. Na²O to the solvent, the rotatory power sinks considerably after some time, and its original value indicates that in alkaline solution milk-sugar exists only as the β -modification (Hesse, *Annalen*, clxxxi. 98). According to Mills and Hogarth (*Proc. Roy. Soc. xxviii. 273*), the initial specific rotatory power of milk-sugar in solution (? dilute) is $[\alpha]_D = 83.16^\circ$, and its permanent specific rotatory power $[\alpha]_D = 53.12^\circ$. They have examined the law for the change of rotation in a freshly prepared solution, and find that it can be expressed by a mathematical equation. The initial solubility of milk-sugar, according to these chemists, is 1 pt. in 10.64 pts. water of 17° , and the permanent solubility 1 pt. in 3.23 pts. water.

3. *Dextrose, Dextroglucose, or Crystallised Grape-sugar*.—Tollens' has examined with great care the rotatory powers of nineteen different solutions of pure dextrose (*Deut. Chem. Ges. Ber. x. 1413*), and finds that the specific rotatory power in solution increases with the concentration; thus in a solution containing 7.68 per cent., the value of $[\alpha]_D$ is 52.89° , while in a solution containing 82.6 per cent. it is 57.8° .

The specific rotatory power in solutions of the anhydrous substance may be calculated from the equations:

$$\begin{aligned} [\alpha]_D &= 52.718 + .017087 p + .0004271 p^2 \\ [\alpha]_D &= 58.69 - .10251 q + .0004271 q^2 \end{aligned}$$

Diminishing these values one-tenth, the following numbers give the rotatory power of the hydrate C⁶H¹²O⁶ + H²O:

$$\begin{aligned} [\alpha]_D &= 47.925 + .015521 p + .0003883 p^2 \\ [\alpha]_D &= 53.362 - .093194 q + .0003883 q^2. \end{aligned}$$

The absolute rotatory power deduced from these equations is:

$$\begin{aligned} [\alpha]_D &= 58.7^\circ \text{ for C}^6\text{H}^{12}\text{O}^6 \\ [\alpha]_D &= 53.36^\circ \text{ ,, C}^6\text{H}^{12}\text{O}^6 + \text{H}^2\text{O} \end{aligned}$$

Hesse (*Annalen*, clxxvi. 102) has determined the specific rotatory powers of several varieties of dextrose at 15° , with the following results:

Glucose-hydrate ^c	Honey-sugar	Grape-sugar	Starch-sugar	Salicin-sugar
1	49.77	—	50.00	50.00
3	47.33	47.87	48.03	48.48
6	46.58	—	46.79	47.96
12	46.34	—	46.83	47.66
Anhydrous	—	51.78 for $c = 2.8$	51.67 for $c = 3$	51.80 for $c = 2.5$

These sugars are therefore identical. Closely allied to them is amygdalin-sugar, which, as hydrate, gives for $c = 2$, $[\alpha]_D = 49.25$. Hydrated phlorizin-sugar, on the other hand, exhibits a smaller rotation, viz. for $c = 3$, $[\alpha]_D = 40.9$, and for $c = 6$, $[\alpha]_D = 40.08$. Another preparation gave for $c = 8$, $[\alpha]_D = 39.9$, and for $c = 10.52$, $[\alpha]_D = 39.7$ (Hesse, *Annalen*, xcii. 174).

The rotatory power of glucose is diminished by the presence of lime. A solution, which in 100 c.c. contained 0.98 grm. lime to 6.9 grm. dextrose, gave for the transition-tint $[\alpha]_J = 33.3$ (Jodin, *Compt. rend.* lviii. 613).

4. Mannitol, $C^6H^{14}O^6$. L. Vignon (*Ann. Chim. Phys.* [5], ii. 433) finds that perfectly pure mannitol is inactive to polarised light. If, however, it be mixed in aqueous solution with boric acid or borates, it becomes dextrogyrate, and a given quantity of borax develops a stronger rotatory power when combined with bases than in the free state. Thus a solution of mannitol containing borax, which originally exhibited a rotation $\alpha = +1.38$, showed, when saturated with carbonate of sodium, potassium, and ammonium respectively, a deflection $\alpha = +5.813$, $\alpha = +6.63$, and $\alpha = +6.73$. The rotatory power increases with time. Arsenic acid and alkaline arsenates likewise develop rotatory power in mannitol. Arsenic acid induces a weak levorotatory power which increases with time. If the solution be then gradually saturated with sodium carbonate, it becomes continually more and more levogyrate. Neutral sodium arsenate induces a dextrorotatory power which does not increase perceptibly with time. Acid potassium arsenate induces levorotation, which likewise increases with time up to a certain limit. Relatively larger quantities of the acid arsenate also develop stronger rotatory powers. On addition of a large quantity of the arsenate, the solution, if left at rest for some time, or more quickly if boiled, becomes perfectly solid, without losing its transparency. The mass thus formed is very friable, easily soluble in water, has an acid reaction, and is strongly levogyrate. From these results Vignon infers that mannitol in itself is active to polarised light. With boric acid and water, without entering into chemical combination therewith—for the evaporated solution leaves a mixture of mannitol and boric acid—it forms dissymmetric molecules which then exhibit rotation. Arsenic and its acid potassium salts, on the other hand, induce a chemical action, in consequence of which the rotations, which are produced only in consequence of unsymmetrical arrangement of the molecules, become altered. The specific rotatory power of mannitol for the transition-tint is, $[\alpha]_J = +36.5^{\circ}$; that of nitromannitol = $+53.26^{\circ}$ (Vignon).

Müntz a. Aubin (*Compt. rend.* lxxxiii. 1213) find that not only borax, but metallic salts in general, and especially the salts of the alkalis and alkaline earths, develop a dextrorotatory power in mannitol, whereas free alkalis develop a levorotatory power. The action is not permanent, for when the salt is removed, the mannitol again becomes inactive or nearly so, and if the alkali be saturated by an acid, the levorotatory power becomes dextrorotatory. Mannitol from various sources was found to be inactive in an aqueous solution containing 10 grams in 100 c.c.; but on addition of 12.8 grams of borax, it gave a mean deviation = $+22.3^{\circ}$. A solution containing in 100 c.c. 8 grams mannitol and 8 sodium hydrate gave a mean deviation = -3.4° . Nitromannitol, 3 grams in 100 c.c. of absolute alcohol, gave a deviation of $+12.4^{\circ}$.

Bouchardat, on the other hand (*Compt. rend.* lxxx. 120; lxxxiv. 34), finds that mannitol in pure aqueous solution is slightly levogyrate, its specific rotatory power for the transition-tint being $[\alpha]_J = -0.15^{\circ}$. Vignon's method of determining it in a solution of mannitol containing borax, is regarded by Bouchardat as fallacious, because chemical compounds are formed in this solution. When acid calcium borate, which is insoluble in water, is added to a solution of mannitol, it is dissolved in the proportion of 1 eq. of the salt to 1 eq. mannitol, and the rotatory power of the very stable compound thus produced is $+28.6^{\circ}$. Caustic soda renders mannitol solution

laevogyrate with a rotatory power of -5.17° . The various ethers of mannitol prepared from glucose or from invert-sugar exhibit, when dissolved in acetic acid, the same rotatory power as the corresponding derivatives of natural mannitol from the ash, and likewise agree with them in other physical properties (see *MANNITOL*, p. 1268).

Glucosides (Hesse, *Annalen*, clxxvi. 116, 125). *Phlorizin*, $C^{21}H^{30}O^{11}.2H_2O$, dissolved in alcohol of 97 v.p.c., gives for $c=1$ and 5, $[\alpha]_D = -(49.40 + 2.41 c)$.

Phloretin, $C^{15}H^{14}O^5$, dissolved in alcohol of the same strength, gave for $c=1$ and 3 no deflection of the plane of polarisation.

Salicin, dissolved in water ($c=1$ to 3), gave $[\alpha]_D = -(65.17 - 0.63 c)$.

Santonin, $C^{15}H^{18}O^3$, in 97 v. p. c. alcohol, ($c=1$ and 2), gave $[\alpha]_D = -173.81^\circ$; in 90 v. p. c. alcohol, -175.4° ; in 80 v. p. c. alcohol, -176.5° ($c=2$ in both cases); in chloroform ($c=2$ to 10), mean value of $[\alpha]_D = -171.53^\circ$, apparently independent of temperature and concentration.

Dichlorosantonin, in 97 v. p. c. alcohol, showed for $c=1$ a rotatory power of only -23° . *Santonin acid*, $C^{15}H^{20}O^4$, at 22.5° in 97 v. p. c. alcohol ($p=1$ and 3) gave $[\alpha]_D = -25.82$, and in 80 v.p.c. alcohol ($c=2$ and 3), $[\alpha]_D = -26.46^\circ$. *Sodium santonate*, at 22.5° in aqueous solution between $p=2$ and $p=10$, gave $[\alpha]_D = -(18.70 \div 0.33 c)$, slightly increasing with the temperature. In 80 v.p.c. alcohol, this salt exhibits the same rotatory power as in water, but on addition of sulphuric acid, the rotation quickly approximates to that of santonin.

Opium Bases (Hesse, *Annalen*, clxxvi. 189). 1. *Morphine*. The *hydrochloride*, $C^{17}H^{19}NO^3.HCl + 3H_2O$, at 22.5° , gave in aqueous solution ($c=1$ to 4), $[\alpha]_D = -(100.67 - 1.14 c)$; in presence of 10 mols. HCl ($c=2$) the value of $[\alpha]_D$ was -94.31 . The *sulphate*, $(C^{17}H^{19}NO^3)_2SH_2O^1 + 5H_2O$, in water at the same temperature ($c=1$ to 4), gave $[\alpha]_D = -(100.47 - 0.96 c)$. The free alkaloid, $C^{17}H^{19}NO^3 + H_2O$, at 25° , in an aqueous solution containing 1 mol. Na_2O ($c=2$), gave $[\alpha]_D = -67.5^\circ$; with 5 mols. Na_2O and $c=2$, the value was -70.23° , and with $c=5$ it was -71.00° .

2. *Codeine*, $C^{18}H^{21}NO^3$, dissolved in 97 v.p.c. alcohol, gave for a solution in which c was between 2 and 8, a rotatory power $= -135.8^\circ$, not influenced by concentration; in 80 v. p. c. alcohol ($c=2$) the value was -137.75° ; in chloroform ($c=2$) it was -111.5° . The *hydrochloride*, $C^{18}H^{21}NO^3.HCl + 2H_2O$, in aqueous solution ($c=2$), gave $[\alpha]_D = -108.18^\circ$, or calculated for the alkaloid, -126.89° ; a solution of the same strength containing 10 mols. HCl gave $[\alpha]_D = -105.22^\circ$; in 80 v.p.c. alcohol ($c=2$) this salt gave -108° . The sulphate in aqueous solution between the temperatures of 15° and 25° gave $[\alpha]_D = -100.9$.

3. *Narcotine*. Experiments were made at 22.5° with the following solvents: Alcohol (97 v. p. c.); the same mixed with 2 vols. chloroform; chloroform; water with 2 mols. and 10 mols. HCl ; 80 v. p. c. alcohol with 2 mols. HCl . The following were the mean results obtained:

	Alcohol	Chloroform	Chloroform	Water	Water	Alcohol
$c=$	0.74	+Alcohol	2 and 5	+2HCl	+10HCl	+2HCl
$[\alpha]_D =$	185.0	-191.5	-207.35	2 and 5 -46.7	2 -50.0	2 -104.5

4. *Hydrocotarnine*, *Meconin*, *Narceine*, and *Cryptopine* were not found to exert any action on polarised light, whatever might be the solvent employed, and even after addition of acids.

5. *Pseudomorphine*. The *hydrochloride*, $C^{17}H^{19}NO^4.HCl + H_2O$, in aqueous solution, acidulated with 1 mol. HCl at 22.5° , gave for $c=0.8$ to 1.6 , $[\alpha]_D = -(114.76 - 4.96 c)$. In a solution ($c=2$) containing 1 mol. pseudomorphine, 5 mols. Na_2O , and 1 mol. $NaCl$, $[\alpha]_D = -198.86^\circ$. For the alkaloid, the value calculated from this result is -235.1° , whereas according to the experiment with the hydrochloride, calculated for $c=2$, the value for the alkaloid is only -123.6° .

6. *Thebaine*, $C^{18}H^{21}NO^3$, dissolved in alcohol of 97 v.p.c., exhibits between $c=1$ and $c=2$ a rotatory power independent of the concentration, but diminishing from -218.6° to -215.5° , when the temperature is raised from 15° to 25° . In a chloroform solution ($c=5$), $[\alpha]_D = -229.5^\circ$. The *hydrochloride*, for $c=2$ to 4, gives $[\alpha]_D = -(168.32 - 2.33 c)$, the value being apparently somewhat diminished by rise of temperature. On addition of 10 mols. HCl , the value of $[\alpha]_D$ is reduced to -158.64° .

7. *Papaverine* dissolved in 97 v. p. c. alcohol ($c=2$), gave $[\alpha]_D = -4^\circ$; in chloroform ($c=5$) it gave -5.7 . The hydrochloride gave no rotation even after addition of free hydrochloric acid.

8. Laudanine, at 22.5° , dissolved in chloroform ($c=2$), gave $[\alpha]_D = -13.5$; in aqueous solution ($c=1$) containing 2 mols. Na_2O to 1 mol. alkaloid, $[\alpha]_D = -11.36^{\circ}$. The hydrochloride gave no rotation either in aqueous, alcoholic, or hydrochloric acid solution.

9. Laudanosine gave the following values:

Solvent	97 v. p. c. Alcohol	Chloroform	Water + 2 mols. HCl
Temperature	15°	22.5°	22.5°
Concentration	$c = 2.79$	2	2
	$[\alpha]_D = +103.23^{\circ}$	105.00°	56.00°
			108.41°

Cinchona Bases (Hesse, *Annalen*, clxxvi. 203-233). All the following determinations were made at the temperature of 15° .

1. Quinine Hydrate, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 + 3\text{H}_2\text{O}$:

In ether (sp. gr. = 0.7296; $c=1.5$ to 6,	$[\alpha]_D = -(158.7 - 1.911 c)$
„ 97 v. p. c. alcohol $c=1$ „ 10	„ $= -(145.2 - 0.657 c)$
„ 80 „ „ $c=1$ „ 6	„ $= -(165.81 - 8.203c + 1.0654 c^2 - 0.04644 c^3)$
„ chloroform + alcohol 2 „ 5	-140.7

The influence of temperature between 15° and 25° lowers the absolute rotatory power, for $c=3$, by 1.56° .

2. Quinine Anhydride, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$:

Solvent	97 v. p. c. alcohol	Chloroform
$c = 1$	2	2
$[\alpha]_D = -170.5$	-169.25	-116.00
		5
		-106.6

Calculation based on the results obtained with the hydrate gives smaller numbers for the anhydride, showing that the entrance of water into the quinine molecule diminishes the rotatory power.

3. Quinine Hydrochloride, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{HCl} + 2\text{H}_2\text{O}$:

In water $c=1$ to 3,	$[\alpha]_D = -(147.31 - 4.96 p + 0.343 c^2)$
„ 97 v. p. c. alcohol, $c=1$ „ 10,	„ $= -(147.30 - 1.9584 p + 0.1039 c^2 - 0.00211 c^3)$
2 chloroform + 1 alcohol, $c=2$	„ $= -126.25$

In mixtures of alcohol and water ($c=2$) the rotatory power rises from -138.75 , its value in pure water, to the maximum -187.75 in alcohol of about 60 v. p. c., and diminishes down to -143.86 in 97 v. p. c. alcohol. In mixtures of water and hydrochloric acid ($c=2$), a maximum $= -225.68$ occurs for 2 mols. HCl to 1 mol. water; with 16 mols. HCl, $[\alpha]_D$ is still $= -209.54$, and in fuming hydrochloric acid -158.75 . The anhydrous hydrochloride gives for $c=0.9$ to 9:

$$[\alpha]_D = - (81.81 - 23.756c + 3.9556c^2 - 0.21981c^3).$$

A rise of temperature of 10° produces no perceptible alteration in the rotatory power of the alcoholic solution.

4. Quinine Sulphates. The *basic sulphate*, $2\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{SH}_2\text{O}^4 + 8\text{H}_2\text{O}$, gives, for $c=2$ in 80 v. p. c. alcohol, $[\alpha]_D = -162.95$; in 60 v. p. c. alcohol, -166.36 ; in a mixture of chloroform and alcohol ($c=1$ to 5), $[\alpha]_D = -(157.5 - 0.27 c)$.

The *monosulphate*, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{SH}_2\text{O}^4 + 7\text{H}_2\text{O}$, gave with water ($c=1$ to 6) $[\alpha]_D = -(164.85 - 0.31 p)$. In other solvents the following values were obtained:

	c	$[\alpha]_D$
Water with 2 mols. SO^3	2	-166.36
„ „ 12 „ „	2	-175.67
„ „ 4 „ HCl	2	-168.25
9 v. p. c. alcohol	2	-134.76
80 „ „	1	-143.63
80 „ „	2	-142.75
60 „ „	2	-155.91
2 vols. chloroform + 1 vol. alcohol	2	-138.75

Quinine Bisulphate, $C^{20}H^{24}N^2O^2 \cdot 2SH^2O^4 + 5H^2O$, in water ($c=2$ to 10), gave $[\alpha]_D = -(170.3 - 0.94 c)$; with addition of 12 mols. SO^3 ($c=2$), $[\alpha]_D = -171.0$, and in 80 v.p.c. alcohol, for $c=1$ and 3 respectively, $[\alpha]_D = -154.54$ and 153.34 .
Quinine Oxalate, $2C^{20}H^{24}N^2O^2 \cdot C^2H^2O^4 + 6H^2O$, dissolved in a mixture of alcohol and chloroform, gave for $c=1$ to 3, $[\alpha]_D = -(141.58 - 0.58 c)$.

5. Cinchonidine gave:

	c	$[\alpha]_D$
In 97 v. p. c. alcohol	1 to 5	- (107.48 - 0.297 c)
" 95 " " "	2 to 5	- (113.53 - 0.426 c)
" 80 " " "	2	- 119.54
" 80 " " "	3	- 116.09
" chloroform-alcohol	2	- 108.86
" " " " "	3	- 108.00
" chloroform. "	2	- 83.66

6. Cinchonidine Hydrochloride, $C^{20}H^{24}N^2O \cdot HCl + H^2O$, gave:

	c	$[\alpha]_D$
In water.	1, 2, 3	- 104.55 103.88 103.03
" " + 4HCl	2	- 151.75
" " + 10HCl	2	- 144.54
" 97 v. p. c. alcohol	3	- 108.00
" 80 " " "	2	- 135.25
" chloroform (anhydrous)	2.85	- 24.21

7. Cinchonidine Sulphates. The *normal salt*, $2C^{20}H^{24}N^2O \cdot SH^2O^4 + 6H^2O$, gave for $c=1.06$, $[\alpha]_D = -106.77$; in 80 v. p. c. alcohol, the salt containing only 3 mols. H^2O ($c=2$) gave -144.54 . The *acid sulphate*, $C^{20}H^{24}N^2O \cdot SH^2O^4 + 5H^2O$, gave ($c=2$) in

	Water	80 v. p. c. Alcohol	Chloroform : Alcohol
$[\alpha]_D =$	-110.5	-109	-101

8. Cinchonidine Oxalate, dissolved in chloroform-alcohol, gave between $c=1$ and $c=3$, for $[\alpha]_D$ a constant value of -98.7 .

9. Quinidine or Conquinine, $C^{20}H^{24}N^2O^2 + 2\frac{1}{2}H^2O$, gave:

	c	$[\alpha]_D$
In 97 v. p. c. alcohol	1 to 3	+ 236.77 - 3.01
" 80 " " "	2	232.72
" chloroform-alcohol	1	244.54
" " " " "	2	241.75
" chloroform (anhydrous)	1.756	230.35

10. Quinidine Hydrochloride, $C^{20}H^{24}N^2O^2 \cdot HCl + H^2O$, gave:

	c	$[\alpha]_D$
In water	1 to 5	205.83 - 4.928 c
" 97 v. p. c. alcohol	2 to 5	212.00 - 2.562 c
" 80 " " "	2	230.25
" water + 1 mol. HCl	2	282.50
" " 4 " "	2	286.00
" " 10 " "	2	278.18
" chloroform-alcohol	2	193.75

The dehydrated salt dissolved in chloroform ($c=2$) gave only 109.25.

Quinidine Dihydrochloride in aqueous solution ($c=2$) gave $[\alpha]_D = 205.33$. In chloroform this salt is nearly insoluble.

11. Quinidine Sulphate, $2C^{20}H^{24}N^2O^2 \cdot SH^2O^4 + 2H^2O$, gave with

c	Water	80 v. p. c. Alcohol	60 v. p. c. Alcohol	Chloroform-alcohol
$[\alpha]_D =$	1	2	2	2
	+ 179.54	218.18	227	209.25

The anhydrous salt dissolved in chloroform gave, for $c=3$ and 5 respectively, $[\alpha]_D = 184.17$ and 180.10 . The *acid sulphate*, $C^{20}H^{24}N^2O^2 \cdot SH^2O^4 + 4H^2O$, gave in:

	c	$[\alpha]_D$
Water	2 to 8	212 - 0.8 c
97 v. p. c. alcohol	2	183
Water with 2 mol. SO^3	2	212.27

Quinidine Oxalate, dissolved in chloroform-alcohol, gave $[\alpha]_D = 189 - 2.18 c$.

12. Cinchonine dissolved in 95 v. p. c. alcohol, in which it is but very slightly soluble, gave $[\alpha]_D = +226.48$; in a mixture of chloroform and alcohol ($c=1$ to 5) it gave $[\alpha]_D = 238.8 - 1.46 c$; if the alcohol in the mixture was only 90 per cent. the rotatory power was 237.27 instead of 235.75.

13. Cinchonine Hydrochloride, $C^{20}H^{24}N^2O.HCl + 2H^2O$, gave in

	c	$[\alpha]_D$	
Water	0.5 to 3	165.5	$- 2.425 c$
97 v. p. c. alcohol	1 to 10	179.81	$- 6.314 c + 0.5406c^2 - 0.0371 c^3$
80 " "	2	188.86	
60 " "	2	195.45	
Chloroform-alcohol	2	152.90	
Water + 4 mol. HCl	2	207.27	
" + 10 "	2	205.50	
Fuming hydrochloric acid	3	206.72	

14. Cinchonine Sulphate, $2C^{20}H^{24}N^2O.SH^2O + 2H^2O$, gave in

	c	$[\alpha]_D$	
Water	0.962 to 1.8312	+ 170.3	$- 0.855 c$
97 v. p. c. alcohol	3 to 10	193.29	$- 0.374 c$
80 " "	2	202.95	
60 " "	2	204.14	
Chloroform-alcohol	2	185.25	

15. Cinchonine Oxalate, dissolved in chloroform-alcohol ($c=1$ to 3), gave $[\alpha]_D = 165.46 - 0.763 c$.

16. Cinchotennine Hydrate, $C^{18}H^{20}N^2O^2 + 3H^2O$, dissolved in chloroform-alcohol ($c=2$), gave $[\alpha]_D = +115.5$, which gives by calculation for the anhydrous base the number 135.5°; in water with 2 mol. SO^2 , the corresponding numbers were 175.5 and 205.9.

The specific rotatory power of the cinchona alkaloids has also been carefully examined by A. C. Oudemans, junr. (*Arch. nêerl.* x. 193). (1). Quinine.—The following are the values obtained for the solution of this base in various inactive liquids, m denoting the number of grams dissolved in 20 c.c. of this solvent:

	Pure Alcohol	Benzene	Toluene	Chloroform	Chloroform
m =	0.328	0.122	0.078	0.293	0.155
$[\alpha]_D$ =	- 167.5	- 136	- 127	- 117	- 1.26

For the solution in pure alcohol, the value of $[\alpha]_D$ at 0° diminishes from $m=0.1$ to $m=1.2$ from 172.3 to 162.4. For the temperature 21°, the corresponding numbers for the same two concentrations are 169.0 and 159.7. Equally variable is the specific rotatory power under otherwise similar circumstances in solutions of 1 molecule = 0.324 grm. in 20 c.c. of aqueous alcohol of various strengths. From the proportion 95 alcohol and 5 water to that of 65 alcohol and 35 water, the value of $[\alpha]_D$ rises steadily from 169.7 to 176.5.

Solutions of quinine salts gave the following results, the specific rotatory power of the salt being denoted by $(\alpha)_s$, and that of quinine itself, as above, by $[\alpha]_D$.

Solution in Pure Alcohol.

	$(\alpha)_D$	$[\alpha]_D$
Normal Sulphate, $(C^{20}H^{24}N^2O^2).SH^2O.1.7\frac{1}{2}H^2O$	- 157.4	- 214.9
Acid Sulphate, $C^{20}H^{24}N^2O^2.SH^2O.1.7H^2O$	- 134.5	- 227.6
Normal Hydrochloride, $C^{20}H^{24}N^2O^2.HCl.2H^2O$	- 138.0	- 169.0
Acid Oxalate, $C^{20}H^{24}N^2O^2.C^2H^2O^4.3H^2O$	- 131.4	- 160.5

Solution in Water.

Acid Sulphate	- 213.7	- 278.1
Normal Hydrochloride	- 133.7	- 163.6

The specific rotatory power of quinine is variously altered by addition of different acids, attaining its maximum in sulphuric, nitric, hydrochloric, and chloric acid, when the quantity of acid added is exactly equal to, or a little less than, that which is required to form an acid salt; with phosphoric and oxalic acids, on the other hand, the maximum is attained only when a larger quantity of acid has been added (4 mol. phosphoric and 3 mol. oxalic); in the case of formic acid, with 28 to 30 mol.

acid; and in that of acetic acid not till 64 mol. acid have been added. In each of those experiments 0.324 grm. quinine was dissolved in the respective quantity of acid, and the solution was diluted with water to 20 c.c. The maxima of rotatory power attained were as follows:

In Oxalic acid	271.7°	In Formic acid	280.6°
" Sulphuric acid	278.8	" Nitric "	284.2
" Acetic "	278.9	" Chloric "	285.7
" Hydrochloric acid	279.2	" Perchloric acid	287.6
" Phosphoric "	280.0		

(2). Quinidine, $C^{20}H^{24}N^2O^2 + 2\frac{1}{2}H^2O$. The solution of 0.324 grm. in 20 c.c. of different solvents gave the following values of the specific rotatory power:

Solvents	Pure Alcohol	Chloroform	Benzene	Toluene
$[\alpha]_D =$	+255.4	+228.8	+195.2	+206.6

At the temperature of 17°, in solutions in pure alcohol, whose concentration varies from 0.1925 to 0.3740, the specific rotatory power decreases from 258.1 to 255.4, but remains nearly constant on further concentration to 0.64. As the temperature rises it becomes somewhat smaller. In mixtures of alcohol and water (always containing 0.324 grm. quinidine in 20 c.c.):

Percentage of water	0	4.7	9.5	15	20	25
$[\alpha]_D =$	255.4	257.6	259.0	259.4	259.3	259.4

Beyond 10 per cent. water, therefore, the variation is but small. The salts of quinidine gave the following results:

Salt	Formula	Solvent	$(\alpha)_D$	$[\alpha]_D$
Sulphate	$(C^{20}H^{24}N^2O^2) \cdot 2SH^2O \cdot 2H^2O$	Pure Alcohol	+211.5°	+255.2°
Nitrate	$C^{20}H^{24}N^2O^2 \cdot NHO^3$	"	199.3	232.6
Hydrochloride	$C^{20}H^{24}N^2O^2 \cdot HCl \cdot 2H^2O$	Water	190.8	244.1
		Pure Alcohol	199.4	233.6
		90.5 p. c. Alc.	213.0	260.7

Quinidine when dissolved in excess behaves almost exactly like quinine, excepting that the maxima do not follow one another quite in the same order.

(3). Cinchonine. The values of $[\alpha]_D$ for this base in alcoholic and chloroform solution, as determined by Oudemans, have been already given (p. 1209). Cinchonine is but slightly soluble in pure alcohol, and its rotatory power does not appear to be affected by the degree of concentration of the solution. In a solution containing 0.1 grm. in 20 c.c., the value of $[\alpha]_D$ is 234.9 at 0°, 224.7 at 15°, 221.1 at 20°. In 90 per cent. alcohol at 17°, $[\alpha]_D = 228.8$. Now Erdmann's *huankine* (iii. 175), under the same conditions, gave 228.0, so that, in this, as in other respects, this base is identical with cinchonine. In chloroform the rotatory power of cinchonine appears to diminish as the concentration increases; in solutions whose concentration is between 0.0914 and 0.1115, the rotatory power varies from +214.8 to 209.6. The influence of various solvents at different degrees of concentration on the rotatory power of cinchonine has already been stated (p. 1209). For medium concentration and temperature, the specific rotatory power of cinchonine in its salts is found by calculation to have the following values:

Salt	Solvent	$[\alpha]_D$
Cinchonine Sulphate	Water	+204.2°
" "	Pure Alcohol	232.9
" Hydrochloride	Water	201.0
	Pure Alcohol	204.4
	93 p. c. "	216.1
	29 " "	229.1
" Nitrate	Water	190.0
	Pure Alcohol	212.2
	93 p. c. "	225.7

A solution of 0.308 grm. cinchonine in 20 c.c. of each of these solvents behaves with excess of different acids analogously to quinine and quinidine.

(4). Cinchonidine. A solution of 0.304 grm. of the pure base in 20 c.c. of pure alcohol exhibited at 0° a specific rotatory power of -112.8° ; a nearly similar solution (0.308 grm.) gave at 17° the value -109.6 . At the latter temperature the value of $[\alpha]_D$ further decreased with increasing concentration, being -108.5 at 0.5182 grm., and -107.8 at 0.771 grm. At the same temperature and a concentration of 0.3 grm. addition of water to the alcohol, from 0 to 40 per cent (by weight) increased the specific rotatory power from -109.6 to -121.1° . In chloroform solution the specific rotatory power of cinchonine is very much diminished by concentration, being -77.4 at a concentration of 0.3089, and -74.0 at 0.6823 grm. The salts of cinchonidine behave in a similar manner. The hydrochloride, nitrate, and sulphate gave at 17° the following values:

Concentration . [α] _D = . .	In Water			In pure Alcohol			In 89 p. c. Alcohol	In 80 p. c. Alcohol
	0.3712 -104.6°	0.4798 102.3	0.6023 99.3	0.3499 99.9	0.5074 97.5	0.6213 96.2	0.3529 119.6	0.3635 128.7

Concentration . [α] _D = . .	Nitrate				Sulphate		
	Water	Pure Alcohol	89 p. c. Alcohol	80 p. c. Alcohol	Pure Alcohol	89 p. c. Alcohol	80 p. c. Alcohol
	0.3377 -99.9	0.3658 103.2	0.3788 119.0	0.3691 127.0	0.34 to 0.38 118.7	0.3622 128.7	0.3686 131.2

Hence it appears that cinchonidine has a greater rotatory power in its salts than in the free state. With acids in excess it behaves like the three other alkaloids. The peculiar behaviour of the four cinchona alkaloids with excess of acid is regarded by Oudemans as connected with their easy decomposibility by water, which probably takes place to a slight extent whenever an acid salt of one of these bases is dissolved in water. It is only by further addition of acid that this decomposition can be prevented, and the entire quantity of alkaloid retained in the form of acid salt, in which its specific rotatory power appears to be a maximum. This point, however, is more quickly attained in proportion as the acid is stronger or combines more readily with the alkaloid.

The results obtained by Oudemans agree well for the most part with those of Hesse, so far as the two admit of comparison, and the differences between them appear to be in most cases due to the circumstance that the alcohol used as a solvent by Hesse was not quite anhydrous. With due attention to all the disturbing causes pointed out by Oudemans, the optical method of investigation may serve, contrary to Hesse's opinion, as a valuable aid in the quantitative analysis of mixtures of alkaloids.

Circular Polarisation induced by Magnetic Action. H. Becquerel (*Ann. Chim. Phys.* [5], xii. 5-88) has determined, by observations on a large number of diamagnetic bodies, the relations which exist between the magnetic rotation of the plane of polarisation of a ray of light and the index of refraction. In the following table, R denotes the magnetic rotation, n the index of refraction, and v the ratio

$$\frac{R}{n^2(n^2-1)}.$$

YELLOW LIGHT (line D).				
Substances	R	n	$n^2(n^2-1)$	v
Fuming Nitric acid	0.206	1.4010	1.8898	0.109
Sulphuric acid, SO^2H^2	0.247	1.4284	2.1225	0.116
" $\text{SO}^2\text{H}^2.3\text{H}^2\text{O}$	0.286	1.4054	1.9156	0.149
Ordinary Nitric acid	0.291	1.3740	1.6760	0.177
Methyl Alcohol	0.253	1.3530	1.5205	0.166
Propyl Alcohol	0.279	1.3836	1.7454	0.160
Butyl Alcohol	0.294	1.3934	1.8247	0.161
Amyl Alcohol	0.311	1.4046	1.9144	0.162
Chloroform	0.380	1.4520	2.3366	0.163
Carbon Monochloride	0.404	1.4580	2.3932	0.169
Xylene	0.525	1.4932	2.7415	0.194
Toluene	0.575	1.4928	2.7375	0.210
Benzene	0.636	1.4998	2.8104	0.226
Melted Sulphur (114°)	1.904	1.9290	10.1268	0.188
Phosphorus Subsulphide	2.592	2.0661	13.9478	0.186
Hydrogen Bisulphide	1.743	1.8850	9.0720	0.192
Sulphur Monochloride	0.984	1.6460	4.6310	0.212
Sulphur Dichloride	0.932	1.6190	4.2493	0.219
Carbon Tetrachloride	0.761	1.5620	3.5128	0.216
Silicon Chloride	0.444	1.4090	1.9561	0.227
Phosphorus Trichloride	0.651	1.5030	2.8974	0.225
Melted Phosphorus (33°)	3.120	2.0740*	14.1558	0.220
Carbon Bisulphide	1.000	1.6240	4.3296	0.231
Arsenic Trichloride	1.000	1.6006	3.9936	0.250
Silver Nitrate, concentrated solution	0.424	1.4580	2.3932	0.177
Bismuth Nitrate, concentrated acid solution	0.452	1.4590	2.4003	0.187
Distilled Water	0.308	1.3340	1.3874	0.222
Potash, concentrated solution	0.464	1.4230	2.0753	0.223
Basic Lead Acetate, concentrated solution	0.375	1.3670	1.6233	0.231
Magnesium Chloride, " "	0.519	1.4300	2.1367	0.243
Hydrochloric acid, " "	0.490	1.4071	1.9401	0.252
Antimony Trichloride, in hydrochloric acid, dilute	0.660	1.4550	2.3647	0.279
Antimony Trichloride, in hydrochloric acid, concentrated	1.435	1.6959	5.3957	0.266
The same (commercial), dissolved in excess of hydrochloric acid	0.703	1.4600	2.4121	0.291
Antimony Pentachloride	1.656	1.5910	3.8762	0.427
Bismuth Chloride, BiCl^3 , dissolved in HCl	1.205	1.5640	3.5369	0.346
Potassium Iodide, concentrated solution	0.801	1.4482	2.2972	0.349
Stannic Chloride	1.035	1.5060	2.8768	0.359
Stannous Chloride, aqueous solution	1.125	1.5272	3.1074	0.362
<i>Melted Substances.</i>				
Borax	0.405	1.5010	2.8230	0.143
Lead Borate, I.	1.405	1.7800	6.8704	0.204
" II.	1.430	1.7800	6.8704	0.209
Glass, No. 8, crown	0.481	1.5260	3.0916	0.155
" 6, flint	0.771	1.5790	3.7220	0.207
" 7, "	0.987	1.6140	4.1810	0.234
Heavy Flint, No. 1	1.360	1.7200	5.8310	0.233
" " 2	1.533	1.7650	6.5360	0.234

* Index according to Dale and Gladstone.

YELLOW LIGHT (<i>continued</i>).				
Substances	R	n	$n^2(n^2-1)$	ν
<i>Single-refracting Crystals.</i>				
Sylvin (Potassium Chloride)	0.672	1.4830	2.6376	0.255
Rock Salt	0.843	1.5430	3.2874	0.256
Blende	5.295	2.3690	25.8836	0.204
Fluor Spar, white I.	0.207	1.4332	2.1634	0.095
" II.	0.234	1.4332	2.1634	0.108
Spinell (coloured by chrome)	0.496	1.7150	5.7085	0.087
Diamond (octohedral)	0.301	2.4200	28.4410	0.010
RED LIGHT (Li) (for Selenium, B line).				
Carbon Bisulphide	1.000	1.6120Li	4.1516	0.240
Cuprous Oxide, crystallised (ziguëlin)	14.060	2.8490	57.7656	0.241
Sulphur Bromide	1.942	1.7630Li	6.2722	0.312
Bromine	1.960	1.6160Li	4.2084	0.465
Selenium Chloride	2.408	1.8070Li	7.2966	0.330
Selenium	10.960	2.6550B	42.6398	0.255

From the numbers in this table the following laws may be deduced :

1. For all diamagnetic bodies, the ratio $R : n^2(n^2-1)$ is comprised within comparatively narrow limits, viz. 0.11 to 0.46, or 1 to 4, whereas the magnetic rotation varies from 0.2 to 14.06, that is from 1 to 70.

2. For bodies belonging to the same chemical family, or composed of the same chemical elements, this ratio is nearly the same; thus the highly oxygenated acids, such as nitric and sulphuric acid, give very small numbers near to 0.11. The fatty alcohols and chloroform give numbers near 0.16. For sulphur, and its compounds with hydrogen and phosphorus, the value is near 0.188; and for the compounds of chlorine with carbon, sulphur, silicon, and phosphorus, it does not differ much from 0.22.

For solutions, the value of $R : n^2(n^2-1)$ is intermediate between that of the solvent and that which would hold good for the dissolved body, and approaches more nearly to the latter as the solution is more concentrated.

In strongly magnetic bodies, such as the salts of iron, if the indices of refraction vary only within narrow limits, the variations of rotation corresponding with the change of refractive index are masked by the great variations dependent on the specific magnetism of the body, which in most cases is strong enough to reverse the direction of the rotation: hence in these bodies there is no apparent relation between the rotation and the index of refraction.

Certain crystallised bodies, as fluorspar, ruby, spinel, and diamond, deviate absolutely from the general law above stated, and exhibit only a very small rotation in proportion to their index of refraction.

In highly dispersive bodies, such as carbon bisulphide and phosphorus monosulphide, the magnitude of the rotation is nearly in the inverse ratio of the square of the wave-length.

• III. CHEMICAL ACTION OF LIGHT.

J. W. Draper (*Sill. Amer. J.* [3], v. 25, 91) has published the experimental evidence forming the basis of his conclusions respecting the distribution of chemical energy in the spectrum (vii. 749). That all the rays of the spectrum are capable of producing chemical action is shown: (1). By the behaviour of silver iodide (on a daguerreotype plate), which, when exposed to the pure spectrum, is affected first and most strongly in the most refrangible parts, but afterwards also in the less refrangible portions. These last-mentioned rays, however, exert a different action if the plate is exposed to the action of faint diffused daylight, either simultaneously with the action of the spectrum or just before it. After the image has been developed by mercury-vapour, it is seen that all the rays of the spectrum have acted on the plate, even the lines α , β , γ in the ultra-red being visible. The finished photograph shows on a light ground an image of the spectrum, the more refrangible portion of which is bluish or olive-coloured, while the less refrangible portion appears deep black with white Fraunhofer lines. The appearance of the plate shows that the more refrangible rays assist the action of diffused daylight, while the less refrangible retard it. (2). By the behaviour of bitumens and resins: when West Indian bitumen

dissolved in light petroleum is irradiated by the spectrum for five minutes and then treated with a mixture of light petroleum and alcohol, an image of the spectrum is formed extending from below A to above H. (3). By the part which light plays in the decomposition of carbon dioxide in plants, which, according to Draper's experiments, is produced chiefly by the rays between B and F, with a maximum in the yellow; the same rays develop the green colouring of leaves. (4). By the decomposing action of light on the colours of flowers, which takes place in such a manner that each colour is destroyed by those rays the mixture of which produces the tint complementary to itself. (5). By the well-known fact that the combination of chlorine and hydrogen is effected by all rays, though in different degrees. (6). By the fact, first observed by Gardner, that when a row of young plants germinated in the dark is illuminated by a spectrum, they all bend towards the one which is illuminated by the indigo-rays, and this latter bends towards the rays themselves.

The statement that a substance is chemically affected by the particular rays which it absorbs, is supported by the following facts: (1). The behaviour of silver iodide. The variously-coloured layers produced by the action of iodine-vapour on a silver plate in different lengths of time, are sensitive to light in very different degrees, each being unaffected by the rays which it reflects, and affected only by those which it absorbs. The sensibility to light depends therefore not only on the chemical but also on the optical nature of the iodide. A certain amount of rays must be absorbed before the action begins, but when once begun, it goes on proportionally to the time. (2). The fact, established by older as well as by recent experiments, that the rays absorbed by chlorine gas are exactly those which induce the combination of chlorine and hydrogen.

P. Chastaing (*Ann. Chim. Phys.* [5], xi. 145-224) has made a large number of experiments on the chemical effect of variously coloured rays on compounds both inorganic and organic, from which he draws the following conclusions: (1). That the action of the differently coloured rays on inorganic bodies varies in kind as well as in degree, according to their refrangibility, the violet and blue, and sometimes also the green rays, exerting a reducing action, the red and yellow rays an oxidising action, and that between the spectral lines D and E, at the boundary of the green and yellow, there is a neutral point, at which the light exerts no chemical action whatever. 2. The chemical action of light on organic bodies is in all cases an oxidising action, increasing from darkness through the red to a maximum in the violet.

These conclusions have however been controverted by H. W. Vogel (*Deut. Chem. Ges. Ber.* x. 1638) by reference partly to Chastaing's own experiments, partly to facts which have long been established. Vogel finds, indeed, that rays of all colours are capable of exerting either an oxidising or a reducing action according to the nature of the body by which they are absorbed, and that the so-called neutral point where, according to Chastaing, no chemical action takes place, has no existence.

That the violet rays do not invariably exert a reducing action is sufficiently shown by the well-known fact that chlorine and hydrogen combine energetically under the influence of these rays; and that, on the other hand, the less refrangible rays can exert a reducing action is shown by Vogel's experiments on chloride, bromide, and iodide of silver, from which it appears that the alteration of these compounds in the red and yellow rays of the spectrum is qualitatively identical with that which takes place in the blue and violet, namely a reduction. The statement that light of all colours exerts an oxidising action on organic bodies is sufficiently refuted by the well-known fact of the decomposition of carbon dioxide by green plants under the influence of light. This process, which is attended with elimination of oxygen, is undoubtedly a reduction, and according to recent experiments by Timiriazeff (*Compt. rend.* lxxxiv. 1236) takes place most rapidly in red light at the chief absorption-band of chlorophyll.

The experiments of H. Vogel on the increase in the sensibility to light of haloïd silver salts produced by addition of optically absorbing substances (vii. 750) have been repeated, with confirmation of their results, by E. Becquerel (*Compt. rend.* lxxix. 185). On mixing a solution of chlorophyll with the collodion of the film of silver bromide or iodide, he obtained, in the red and yellow regions of the spectrum, several maxima of action, the strongest of which, situated between B and C, corresponded nearly with the principal absorption-band of chlorophyll; the others, between C and D, with the other absorption-bands of that substance.

Further experiments by Vogel (*Pogg. Ann.* cliii. 218; *Deut. Chem. Ges. Ber.* vii. 545, 976) on the sensibility of the haloïd salts of silver to light have led to the following results: (1). Chloride, bromide, and iodide of silver are sensitive, not only to the more refrangible, but also, though in a far inferior degree, to the less refrangible rays of the spectrum. (2). The sensitiveness of silver haloïd salts to the different spectral colours depends, not only on their optical absorption-capacity for these rays,

but likewise on the optical absorption-capacity of admixed substances. (3). Coloured bodies—naphthalene-red, for example—which assist the photographic reduction process, and at the same time absorb certain spectral colours, give rise, when properly applied, to a great increase in the sensitiveness of silver salts to the absorbed rays. In this way, the sensitiveness of silver salts to the red, yellow, and green rays may be greatly heightened. (4). Mixtures of different colouring matters produce an effect equal to the sum of the effects of their several constituents. (5). Certain colourless bodies also (*e.g.* silver nitrate and morphine) which promote photographic reduction, exert a considerable modifying influence on the colour-sensitiveness of silver salts. (6). The photographic action of absorbent substances exhibits a certain analogy to anomalous dispersion (vii. 742), inasmuch as the sensitiveness increases or diminishes with the index of refraction. Hence perfectly indifferent bodies, collodion, for example, which influence the index of refraction, displace both the absorption-band and the point of strongest photographic action. (7). The action of light reflected from coloured pigments is very different from that of the spectral colours, being affected not only by the optical composition of the pigment colours, but likewise by their far inferior brightness.

The third of these laws respecting the effect of coloured bodies on the sensitiveness of silver haloid salts has been called in question by M. Carey Lea (*Sill. Am. J.* [3], vii. 200; ix. 355), who points out especially that, according to this law, naphthalene and corallin ought to increase the sensitiveness of silver bromide to the green rays, whereas Vogel found that they gave increased sensitiveness only for the yellow rays. According to Lea, corallin greatly increases the sensitiveness of silver bromide for the red rays, moderately for the yellow, and not at all for the green. Vogel finds by further experiments (*Deut. Chem. Ges. Ber.* viii. 95, 1635) that different silver salts are variously affected by one and the same colouring matter. Naphthalene-red added to silver bromide increases its sensitiveness to the yellow, and produces a similar and greater effect on the chloride. Fuchsin acts with silver bromide in a manner exactly corresponding with its absorption, and almost in the same way as naphthalene; with silver chloride it does not greatly increase the sensitiveness to any rays except the violet. A similar behaviour is exhibited by colourless bodies, like morphine, which increases the action on silver bromide in the green, blue, and violet, but has no effect on the bromide. Pyrogallol acts nearly in the same manner.

The following conditions are laid down by Vogel as necessary to insure the conformity of a colouring matter to his law above mentioned: (1). It must optically absorb that particular kind of light for which it is to make the collodion sensitive. (2). It must be capable of combining chemically with free bromine or iodine. (3). It must not decompose silver nitrate, as in that case it would interfere with the preparation of the plates.

Methyl-violet and cyanine were found to strengthen the action on silver bromide of the rays which they absorb, the latter intensifying the action of the orange-rays in a very high degree; picric acid, aniline-blue, night-blue, pensée-lac, indigotin, and purpurin, on the contrary, did not exhibit any such intensifying action. The coloration of a film of silver bromide by colours which are destroyed by the action of free acids in the collodion or in the silver-bath may be most readily effected by wetting the prepared bromide of silver plates with an alcoholic solution of the colouring matter, and leaving them to dry.

Vogel also finds (*Ber.* ix. 667) that silver bromide (like the iodide) exhibits a very different degree of sensitiveness to light, accordingly as it has been precipitated with excess of silver nitrate or of potassium bromide. The bromide by itself is much more sensitive than the iodide, but its sensitiveness is not increased by the action of intensifying substances, whereas all such bodies heighten the sensitiveness of the iodide in a very great degree. Plates prepared with excess of potassium bromide showed no action in the yellow, whereas when immersed in a bath of silver nitrate and then coated with naphthalene-red, they became sensitive to yellow light. A similar effect was produced by cyanine. Vogel accordingly draws a distinction between bodies which increase the sensitiveness of silver bromide or iodide by their power of optical absorption, and those which, like tannin, act chemically by combining with the bromine or iodine.

According to Carey Lea (*Sill. Am. J.* [3], xi. 459; xii. 48), the optical absorbing power of sensitising substances has very little to do with their property of rendering silver bromide sensitive to rays of lower refrangibility. Of fourteen red colouring matters examined, corallin alone rendered that compound sensitive in the green, which effect, however, cannot be due to its power of absorbing the green rays, since it renders the silver bromide still more sensitive to the red rays which it transmits; moreover, its sensitising action is not destroyed by the action of acetic or gallic acid, which turns it yellow. The following colouring matters, which are more or less non-absorbent

for the green rays, nevertheless heighten the sensitiveness of silver bromide for these rays: potassium arsenite, silver arsenite, salicin, codeine, morphine acetate, tincture of capsicum, ammonium valerate, and caffeine (?) Many alkaloïds diminish the sensitiveness for the green. The only body which acts nearly in accordance with Vogel's law is chlorophyll.

Lea has also examined the sensitiveness of a number of silver-salts to light, chiefly with the view of ascertaining which of them, besides the chloride, bromide, and iodide, can be used for photography. Paper was impregnated with soluble salts of acids capable of forming insoluble compounds with silver, then floated on the surface of silver nitrate; some of the paper was also treated with gallotannic acid. It was then exposed to diffused light for seven to twelve seconds, and the image developed by pyrogallol, ammonium carbonate, and potassium bromide. None of the substances examined gave strong images, with the exception of the platinoeyanide and the arsenite. Tannin was not found to exert any beneficial action (*Sill. Am. J.* [3], xiii. 369).

Photographing of the Ultra-red and Violet Rays.—J. Waterhouse (*Proc. Roy. Soc.* xxiv. 186) has obtained reversed photographs of the extreme red and ultra-red rays of the solar spectrum on silver bromide collodion plates, which were exposed for a second to diffused daylight before being subjected to the action of the spectrum. The blue and violet rays between F and H were also frequently reversed on silver bromide plates coloured and uncoloured, after prolonged exposition.

Waterhouse also finds that silver bromide plates, coloured with eosin, are most sensitive to the green and yellow rays, a fact which accords with Vogel's theory; for the pigment, when dissolved in water or alcohol, is of a light orange-red colour with greenish-yellow fluorescence. The absorption-spectrum of the dilute aqueous solution shows a darkening from below E to above F. Plates coated with bromide of silver exhibited only a slight increase of action in the green and yellow. For the photographing of coloured objects, plates thus coloured were found to be not well adapted, on account of the retardation of the action consequent on the colouring.

Production of Coloured Spectra by the Action of Light.—Examples of the production of natural colours by the agency of light were shown some time ago by Becquerel; and Captain Abney, in a paper lately communicated to the Royal Society (June 19, 1879), reports that he has succeeded in obtaining coloured pictures of the solar spectrum both on silver plates and on compounds of silver held in position by collodion. The spectrum imprints itself in approximately natural colours, which are more brilliant on the silver plate than on the collodion film, but those on the latter can be seen by transmitted as well as by reflected light. These colours are produced by oxidation of silver-compounds placed in the spectrum, an exposure of two minutes with a wide slit being sufficient for their development (*Chem. News*, xxxix. 282).

Action of Light on Potassium Iodide.—Vidan (*Pharm. J. Trans.* [3], v. 383, 393) observes that a neutral solution of potassium iodide is decomposed by bright sunshine. The pure solution turns yellow from separation of iodine; paper soaked in solution of potassium iodide and starch-paste, and sealed up in a glass tube, is turned bright blue when exposed to sunshine for an hour. On this account the use of iodised starch-paper as a test for ozone may lead to very uncertain results, as formerly pointed out by Cloez (*Compt. rend.* xliii. 38) and by Campani (*Cimento*, iv. 112).

On the Decomposition of Hydrogen Iodide by Sunlight, see CHEMICAL ACTION (p. 429).

Action on Vanadium Salts.—Acid potassium vanadate, in contact with organic substances, is turned by light first green and finally blue; when not in contact with organic matter it is unaffected by light. Neutral sodium vanadate laid on glass in a colourless film and exposed to sunshine is somewhat browned, but becomes colourless again when left for some hours in the dark and in a draughty place. Paper moistened with its solution acquires a slate colour, and if then dipped into solution of silver nitrate, instantly becomes dark brown to black, according to the time of exposure. This salt may therefore be used for photography.

Action on Sulphurous Acid.—Dilute solutions of sulphurous acid, exposed to sunshine for a whole summer in sealed glass tubes, remained clear for two months, but afterwards exhibited a continually increasing turbidity, sulphur being separated and the liberated oxygen converting the remaining sulphurous acid into sulphuric acid. Solutions of sulphuric acid, sulphates, and sulphites, under similar circumstances, showed no sign of alteration.

Action of different rays on Chlorophyll.—The following experiments have been made by J. Wiesner (*Pogg. Ann.* clii. 496; cliii. 622) with reference to the much

disputed question as to which rays of the spectrum are most active in the decomposition of chlorophyll. Equal and similarly disposed quantities of chlorophyll-solution were subjected to the action of rays which had passed through equally thick layers, either: (1) of a white turbid liquid (water in which calcium oxalate was suspended); or (2) of a yellow solution of potassium dichromate; or (3) of a green ethereal solution of chlorophyll; or (4) of a red solution of æsculin-orcein; or (5) of a blue solution of cuprammonium sulphate, particular care having been taken to make the five solutions equally transparent. It was found that the action was strongest when the light had passed through the first medium, and diminished for each of the successive media in the order above stated, so that the yellow rays from C to E must be regarded as the most effective, a result likewise obtained by Pfeffer (*infra*). Xanthophyll, however, which, when an alcoholic solution of chlorophyll is shaken up with light petroleum or carbon sulphide, alone remains dissolved in the alcohol, is most quickly decomposed by rays which have passed through cuprammonium sulphate. Wiesner infers from his experiments that the decomposition of dissolved chlorophyll under the influence of light is an oxidation process from beginning to end, whereas Gerland regarded the presence of oxygen as necessary only to start the action (vii. 327).

E. Lommel (*Pogg. Ann.* cxliii. 568; cxlv. 142) infers, from experiments on the influence of coloured light in promoting the decomposition of carbon dioxide by plants, that this action is greatest for the rays which correspond in refrangibility with the absorption-band of chlorophyll between B and C. Pfeffer, on the other hand (*ibid.* cxlviii. 86), disputes this conclusion, and finds that the curve of decomposition has its maximum in the yellow, and descends regularly on both sides from that point. His experiments were made by exposing a green plant (*Elodea Canadensis*) in a glass tube filled with water to the several parts of a spectrum formed by light passing through a slit 5 mm. wide, and counting the gas bubbles evolved in given time. More exact experiments have however been made by Timirjaseff (*Ann. Chim. Phys.* [5], xii. 255), who exposed strips of bamboo-leaf of equal width contained in narrow test-tubes, and enclosed in an atmosphere containing 5 per cent. CO_2 , to the action of the several parts of a spectrum produced with a slit only 1 mm. broad and a prism of carbon disulphide, and subjected the gases evolved after five hours' insolation to a very careful analysis. The result of his experiments is to show decidedly that the maximum decomposition is produced by the rays corresponding with the characteristic absorption-band of chlorophyll in the red, and that the rays for some distance before E (yellowish-green) have no influence whatever. The contrary results obtained by Pfeffer are attributed by Timirjaseff to the necessarily impure spectrum obtained with an aperture 5 mm. wide, and to the inexact measurement of the products of decomposition. The same part of the spectrum appears also to correspond with the greatest mechanical energy of the luminous vibrations; moreover, absorption-bands are produced in this neighbourhood by carbon dioxide and water-vapour. The fact that blue and violet light, which are likewise absorbed by chlorophyll, nevertheless exert no influence on the assimilative power of plants, requires special explanation, which has not yet been obtained.

Measurement of the Chemical Intensity of Sunlight.—E. Marchand (*Ann. Chim. Phys.* [4], xxx. 302; *Monit. Scient.* [3], vi. 979) uses for this purpose a mixture of ferric chloride and oxalic acid in equivalent proportions, which, under the influence of insolation, is decomposed as represented by the equation:



The quantity of carbon dioxide evolved in a minute corresponds with a certain quantity of heat evolved (according to Favre, the oxidation of 1 gram of oxalic acid evolves 670 gram-degrees), and this is regarded by Marchand as a measure of the chemical power of the solar rays. The solution is most strongly decomposed by the blue rays between F and G, the action diminishing much more slowly towards the red than towards the violet end. When the liquid is in constant contact with a horizontally exposed surface of glass, the number of c.c. of carbon dioxide evolved per square centimeter is expressed, for a mean sun's altitude h , by the formula

$$m = 0.00092300 + 0.00000729(h-1).$$

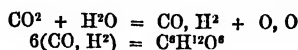
When the rays are reflected constantly at right angles to the surface by a heliostat, the expression becomes

$$m' = 0.001394 + 0.000002(h-1).$$

These numbers are true for the sea-level at Fécamp on the Channel for a perfectly clear sky. The chemical irradiations are not altered by wind, but are affected by clouds, brightly illumined cirri and cumuli increasing the reaction. By this method

Marchand has drawn up tables representing the chemical climate of Fécamp. E. Becquerel, however, observes that these tables can have only a relative value, and cannot afford a true measure of the chemical energy of the rays, inasmuch as rays which have no action on the particular liquid employed might be capable of exerting a very powerful action on other liquids.

J. Dewar (*Phil. Mag.* [4], xliv. 307) has calculated, from Boussingault's measurements of the decomposition of carbon dioxide by the leaves of plants (*Ann. Chim. Phys.* [4], xiii. 415), the fraction of the total energy of the solar rays received on a unit of leaf-surface, which takes the form of chemical energy. Starting from the two formulæ,



and the thermal equivalents, $\text{CO}, \text{O} = 68000$; $\text{H}_2, \text{O} = 68000$; glucose, $\text{C}^6\text{H}^{12}\text{O}^6 = 642000$ (the last said to have been determined by Frankland), he calculates as follows: According to the first formula, the decomposition of 1 c.c. CO_2 requires 6.06 gram-degrees of heat. If, however, the products of decomposition become condensed, as represented by the second formula, the quantity of heat required will be only

$6.06 \times \frac{642000}{6(68000 + 68000)} = 4.78$; and since, according to Boussingault, 1 square centimeter of leaf-surface assimilates in an hour 5.28 c.c. CO_2 , while on the other hand Pouillet estimated the amount of energy radiated by the sun in the latitude of Paris on 1 square centimeter of normally exposed surface at 6000 gram-degrees, it follows that the chemical energy of light is $\frac{4.78 \times 5.28}{6000} = \frac{1}{238}$ of the total energy.

LIGNITE. A lignite from Disco Island, on the west coast of Greenland, has been analysed by H. Wurtz (*Amer. Chemist*, iv. 401). The substance desiccated in dry winter air contained 14.00 per cent. water, 35.38 volatile matter, and 50.62 coke (= 41.79 carbon and 8.83 ash). When ignited even in a covered crucible, it emits a dull yellow, smokeless, feebly luminous flame. It gives off water at the heat of a sand-bath, and contracts strongly at higher temperatures, yielding an anthracitic coke, the volume of which is about 40 per cent. less than that of the original coal. The ash of the coke, which has a green colour, due to manganese, melts at high temperatures to a dark-coloured glass; it does not contain carbonic acid. The lignite has a very high specific gravity = 1.452–1.468; that of the coke is 1.836. The coke contains also a large quantity of occluded gas, which it does not give off completely till it has been boiled for half-an-hour.

On the composition of lignite from Toula in Russia, see p. 526.

On the gases enclosed in lignite from Bovey Heathfield, see p. 534.

LIMBACHITE. A hydrated silicate of aluminium and magnesium, occurring in clefts of the serpentine of Limbach. A and B. Analyses. C. Numbers calculated from the formula $3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$:

	SiO^2	Al_2O^3	Fe_2O^3	MgO	H_2O	Sp. gr.
A.	41.42	22.09	undet.	23.67	12.47* = 99.65	} 2.395
B.	42.03	19.56	1.46	25.61	12.34 = 101.00	
C.	39.38	22.54	--	26.26	11.82 = 100	

(A. Frenzel, *Jahrb. f. Min.* 1873, 789).

LINARITE. This mineral occurs in the Ortiz mine, Sierra de las Capillitas, Argentine Republic, together with malachite, azurite, cerussite, brochantite, and anglesite (A. Stelzner, *Min. Mitt.* 1873, 249). An analysis by Frenzel (*Jahrb. f. Min.* 1875, 675) gave:

CuO	H_2O	PbSO^4	Sp. gr.
20.22	4.69	74.42 = 99.33	5.06 at 17°.†

LINSEED MUCILAGE. See MUCILAGE.

LINSEED OIL. An adulteration of this oil with cod-liver oil may be detected by stirring up 10 grams of it with 3 grams of commercial nitric acid, and leaving the mixture at rest till the oil and acid have separated. Pure linseed oil thus treated exhibits first a sea-green, then a dirty yellow-green colour, while the acid acquires a light yellow colour. If, on the other hand, cod-liver oil is present, the oil becomes dark-brown to black, the acid orange-yellow to yellow-brown (*Dingl. pol. J.* ccxv. 284).

On the preparation of Linseed-oil varnish and of Varnish-paper, see E. Thorey (*Dingl. Pol. J.* ccxiv. 427; *Jahresh. f. Chem.* 1874, 1197).

* At 100° = 4.4 per cent.

† Stelzner found 5.23 at 16°.

LIQUIDAMBAR. W. L. Harrison (*Arch. Pharm.* [3], vi. 541) obtained from the balsam of *Liquidambar styraciflua*, cinnamene, cinnamic acid, styracin, and a dark-brown, nearly scentless and tasteless resin, easily soluble in alcohol, insoluble in carbon sulphide.

J. M. Maisch (*ibid.* 545) infers from the results of Harrison's investigations that the balsams of *Liquidambar styraciflua* and *L. orientale* are identical, and ascribes their difference of external aspect to the presence of water in the balsam from *L. orientale*. To obtain pure styracin (cinnyl cinnamate, $C^9H^7O^2.C^9H^7$) and cinnamic acid from the balsam, Maisch recommends extraction with petroleum-ether, whereby a solution is obtained, which deposits a mixture of the two substances, separable by ammonia.

LIQUIDS. *Absorption by Charcoal.*—The absorption of water, alcohol, ether, carbon sulphide, and bromine by charcoal is attended with considerable evolution of heat. 5 to 10 grams of charcoal in contact with a 7 to 9-fold quantity of bromine produced a rise of temperature exceeding 30° . The volatile liquids thus condensed in the pores of the charcoal are only partially expelled, or not at all, at 100° (Melsens, *Compt. rend.* lxxvii. 781).

On the Compressibility of Liquids, see Amagat (*Ann. Chim. Phys.* [5], xi. 520–549; *Jahresb. f. Chem.* 1877. 71).

Capillarity.—G. Quincke, in connection with his former observations on the phenomena of capillarity at the surface of contact of two liquids (vii. 240–243), has investigated the edge-angle at the contact of a liquid and a solid, and the spreading out of liquids on the surface of solid bodies (*Ann. Phys. Chem.* [2], ii. 145–194). The results are stated in the following propositions: (1). The known properties of the surface of contact of two liquids may be extended to that of a liquid and a solid. (2). The contact-surface of a solid 1 and a liquid 2 tends to become as small as possible, or there prevails in it a certain surface-tension, $\alpha_{1,2}$, independent of the geometrical form of the surface, and dependent only on the nature of the substances 1 and 2. (3). The magnitude of the edge-angle of a solid 1 and a liquid 2, both bounded by a liquid 3, is determined by the nature of the three substances, and is independent of the geometrical form of the surface. (4). The main proposition of the theory of capillarity, established by Thomas Young, respecting the constancy of the edge-angle of the free surface of a solid and a fluid is a particular case of the preceding theorem (3), the fluid 3 consisting of the air. (5). The edge-angle may be deduced by calculation from the measurement of the surface of flat drops and bubbles, or measured directly by reflected light. (6). The edge-angle of the free surface of different liquids such as water, alcohol, &c., and of aqueous or alcoholic salt-solutions towards clean surfaces of glass, quartz, or metal, appears to be equal to 0° , the liquids spreading freely on the clean surface of the solid. (7). If the edge-angle, as in most cases, has a greater value, the surface of the solid becomes coated with an imperceptibly thin layer of foreign substance, the edge-angle varying with the thickness of the layer. (8). The thickness of this layer cannot, however, exceed a certain maximum value D , which is equal to or greater than the radius of the sphere of action of the molecular forces. (9). This thin layer adhering to the surface of the solid body may consist either of solid, or of liquid, or of gaseous substance. (10). It may consist of the liquid itself, which is in contact with the solid, and may be recognised, not only by the edge-angle, but also by the so-called 'creeping' of salts, or by the rate of electric conduction on the surface of the solid,—in some cases also by the interference-colours of the light reflected from it. (11). These imperceptibly thin layers of liquid differ in properties according to the mode of their production, and the length of time occupied therein, or according to the nature of the bodies to which they adhere. Quickly formed drops of water spread out on freshly cleaned surfaces of glass more quickly than those which have been slowly formed. (12). These imperceptibly thin films of foreign substance appear also to afford an explanation of the differences between theory and experiment in the estimation of the surface-tension at the common boundary of liquids and solids. (13). If the edge-angle is equal to 0° , or impossible, the liquid spreads out on the surface of the solid body. (14). In liquids which mix together in all proportions, that which has the smaller surface-tension, $\alpha_{1,2}$, displaces that which has the greater surface-tension, $\alpha_{1,3}$. The surface-tension and the possible displacement vary, however, with the nature of the solid substance. (15). The presence of other fluids, and especially of air, may essentially modify the spreading of a liquid on the surface of a solid. (16). The dependence of the edge-angle on the thickness of the imperceptibly thin film on the surface of a solid explains the breath-pictures of Moser (*Pogg. Ann.* lvi. 177; lvii. 1) and Waidele (*ibid.* lix. 255) with water-vapour; the light-pictures of Daguerre with mercury-vapour (*Compt. rend.* ix. 257), and the

electric breath-pictures of G. Karsten (*Pogg. Ann.* lvii. 493) and Riess (*Reibungs-elektricität*, ii. 224), with the vapours of water, mercury, and iodine.

Quinke further observes that a glass surface can never be perfectly cleaned by rubbing it with a linen cloth and alcohol, or by prolonged immersion in alcohol. The best way of proceeding is to treat the glass with hot strong sulphuric acid, then rinse it with distilled water, leave it immersed in water for a long time to remove the last traces of acid, and dry it in the warm current of air over the colourless flame of a Bunsen lamp. It must then be left to cool on a clean clock-glass in a clean glass vessel covered with a glass plate. *Metals* are still more difficult to clean than glass. Noble metals may be ignited in a colourless Bunsen flame and left to cool in clean covered vessels.

The *creeping* or *efflorescence* of salts is commonly attributed to the rise of the solution between the salt already crystallised out and the side of the vessel. The formation of the first crystals, which often takes place on a part of the solid surface at a considerable distance from the liquid, is, however, determined by the imperceptibly thin film of salt-solution which covers the surface of all solid bodies, as metals, glass, quartz, &c. When a portion of the water evaporates, a fresh portion of the salt solution flows in beneath the thin film. The thickness of the film and the quantity of salt solution which thus flows out are greater in proportion to the degree of cleanliness of the solid body. Crystals of the salt form on that part of the surface where the water evaporates most quickly, that is to say at the outer edge of the liquid film. The surface of the solid body often exhibits different degrees of cleanliness on different parts, and then the crystals form first on the cleaner places, and at a greater distance from the flat drop of liquid, than on the less clean parts. If the surface of the solid body is covered with a thin layer of oil, no efflorescence takes place. Since glass surfaces, when exposed to the air, remain clean longer than metal surfaces, salts mostly effloresce on them more readily than on metal surfaces. For the rest, efflorescence or creeping will be most readily exhibited by those salts which, when sufficiently concentrated, still remain mobile—that is to say, the least viscid salts will, under otherwise similar conditions, effloresce with the greatest facility.

Tension and Capillary Constants of Liquid Films.—The following table exhibits the results obtained by Sondhauss (*Pogg. Ann.* Ergänzbd. viii. 266) respecting the tension and capillary constants of liquid films formed in rings of wire. The experiments on the first two liquids were made at the temperature of the air :

	Tension for the space of 1 mm.	Capillarity-constant thence deduced	Observed capillary height for 1 mm. radius	Capillarity-constant thence deduced
<i>Soap solution :</i>				
1 : 100	5.27 mg.	2.63 mg.	5.38	—
1 : 1000	5.25	2.62	5.64	—
1 : 3000	5.47	2.73	6.61	3.3
<i>Saponin solution :</i>				
1 : 1000	11.76	5.88	12.41	6.20
1 : 10000	13.66	6.83	14.32	7.16
1 : 20000	14.22	7.11	14.45	7.22
<i>Water :</i>				
Temperature				
1.6°	15.53	7.76	—	—
3.6	15.35	7.67	—	—
5.0	15.25	7.62	—	—
16.6	14.86	7.43	—	—
<i>Mercury :</i>				
Temperature				
0°	—	53.85	—	—
7.5	—	51.73	—	—
18.2	—	49.67	—	—
25	—	47.8	—	—

Obermayer (*Pogg. Ann.* cli. 130) describes the radiate spreading out of strong solutions of aniline-dyes in commercial aniline on water, and finds therein a confirmation of the view advanced by Monsbrugge (*ibid.* cxxxviii. 323; *Jahresh. f. Chem.* 1869, 39) that the tension on the surface of a liquid is diminished by placing on it a

drop of another liquid of inferior surface-tension, which gives rise to a movement of the superficial particles in the direction of those portions where the original tension exists.

On the Forms of Equilibrium of Liquid Masses, see Plateau (*Compt. rend.* lxxviii. 38).

On the Surface-viscosity of Liquids (Plateau, *Institut.* 1873. 22; *Chem. News*, xxvii. 161; *Jahresh. f. Chem.* 1873. 25). On the Vibrations of Liquid Surfaces of Definite Form, &c., Barthélemy (*Ann. Chim. Phys.* [5], i. 100-122).

On the Movements of Camphor and of certain Liquids on the Surface of Water, see Tomlinson (*Pharm. J. Trans.* [3], iv. 654, 672).

On the Diffusion of Saline Solutions, see Johannisjanz (*Ann. Phys. Chem.* [2], 15 24-47; *Jahresh. f. Chem.* 1877. 80).

Velocity of Efflux from Capillary Tubes.—A. Guerout (*Compt. rend.* lxxix. 1201) has determined the influence of temperature on the rate of capillary efflux. The values for water, given in the following table, show the number of cubic millimeters run out in a second:

Temperature of the water	Coefficient of efflux	Temperature of the water	Coefficient of efflux
10°	3045	16°	3525
11	3110	17	3615
12	3190	18	3703
13	3270	19	3795
14	3350	20	3890
15	3440		

These numbers form a geometric series with the common ratio 1.025; for a solution of potassium sulphate of 10° B. the ratio is 1.026; for potassium carbonate of 43° B. it is 1.046. Considering the rapid decrease of mobility in the molecules of a liquid as the temperature falls, the arrest of circulation in the capillary tissues of the organism in consequence of frost may be due, not to freezing, but to a partial annihilation of mobility.

Guerout (*Compt. rend.* lxxxiii. 1291) has also determined the following efflux coefficients.

Acids.

Formic acid, CH_2O_2	115.0
Acetic, $\text{C}^2\text{H}^4\text{O}_2$	160.5
Propionic, $\text{C}^3\text{H}^6\text{O}_2$	189
Butyric, $\text{C}^4\text{H}^8\text{O}_2$	129.5
Valeric, $\text{C}^5\text{H}^{10}\text{O}_2$	92.3
Caproic, $\text{C}^6\text{H}^{12}\text{O}_2$	64.0

Ethers.

Ethyl Formate, $\text{C}^3\text{H}^6\text{O}_2$ 542.0	Methyl Acetate, $\text{C}^3\text{H}^6\text{O}_2$ 534.5
" Acetate, $\text{C}^4\text{H}^8\text{O}_2$ 450.3	Ethyl, $\text{C}^4\text{H}^{10}\text{O}_2$ 450.3
" Propionate, $\text{C}^5\text{H}^{10}\text{O}_2$ 360.3	Propyl, $\text{C}^5\text{H}^{12}\text{O}_2$ 362.8
" Butyrate, $\text{C}^6\text{H}^{12}\text{O}_2$ 297.0	Butyl, $\text{C}^6\text{H}^{14}\text{O}_2$ 305.3
" Valerate, $\text{C}^7\text{H}^{14}\text{O}_2$ 241.3	Amyl, $\text{C}^7\text{H}^{16}\text{O}_2$ 230.2

For all ethers, the coefficient of capillarity efflux is much greater than for the alcohols and acids from which they are formed. Isomeric ethers exhibit among themselves the same state of fluidity, which however is different from that of the acids which are isomeric with them.

Expansion of Liquids consequent on the Absorption of Gases.—J. Mackenzie and E. Nichols (*Ann. Phys. Chem.* [2], iii. 134) have determined the expansion thus produced, by exactly filling a vessel with the liquid to be examined, connecting it with a second vessel, and passing in the gas till the liquid is completely saturated. The portion which overflows into the second vessel is then weighed, as also that which remains in the first vessel.

The following table gives the average coefficients of expansion for water and carbon dioxide thus determined:

Temperature	Coefficient	Temperature	Coefficient
2°	0·002144	17°	0·001240
6	0·001726	18	0·001280
8	0·001670	22	0·001210
12	0·001150	27	0·001190
14	0·001379	32	0·001010
16	0·001378		

On comparing these results with the coefficients of absorption, as given by Bunsen, it is seen that the expansion is directly proportional to the amount of gas absorbed. The density of the absorbed carbonic anhydride is found to approximate closely to the value given for the liquefied gas by Andrews (*Phil. Mag.* [5], i. 78).

The expansion by heat of water saturated with carbon dioxide was determined in a glass vessel having a narrow glass tube dipping into mercury. The vessel filled with the saturated aqueous solution of the gas was cooled about 2°, and the amount of mercury which passed into the narrow tube was determined. The following table was thus obtained:—

Temperature interval	Average temperature	Coefficient
4·0 — 1·90°	2·95°	0·0000604
5·8 — 3·40	4·6	0·0000610
7·4 — 4·80	6·1	0·0000679
12·15 — 9·85	11·0	0·0000999
12·85 — 11·21	12·03	0·0001130
16·50 — 12·75	14·62	0·0001252
20·60 — 16·4	19·0	0·0001710
23·43 — 20·33	21·88	0·0001811
25·3 — 23·46	22·88	0·0002170
27·55 — 25·0	26·27	0·0002526
29·15 — 26·32	27·73	0·0002923
31·7 — 28·73	30·21	0·0002680

On the Conducting Powers of Liquids for Electricity and Heat, see pp. 723–725 and 1018.

Experiments by Tollinger on the Electric Resistance of solutions of sulphuric acid and various salts to the passage of constant and varying voltaic currents, have yielded results agreeing very nearly with those of Kohlrausch (p. 723), and have shown further that the values obtained with constant and with induction currents do not exhibit any material differences (*Ann. Phys. Chem.* [2], ii. 510; *Chem. Soc. J.* xxxiv. 103).

On Liquids enclosed in Mineral Cavities, see FLUID CAVITIES (p. 793).

Separation of Mixed Liquids.—A homogeneous mixture of two liquids may often be separated into two layers by a slight change of condition, such as a fall of temperature. Whatever may have been the composition of the mixture, that of the two layers thus formed is constant, their relative volume alone varying. The same statement holds good in the case of three liquids where the third is uniformly distributed in both layers.

In certain cases a variation of 0·1° C. will cause separation. For example, a mixture of 15 c.c. of amyl alcohol, 20 c.c. of ethyl alcohol, and 32·9 c.c. of water remains homogeneous at 20°, but with the slightest fall of temperature it divides into two layers, which do not reunite unless shaken up. By varying the quantity of water, the temperature of separation may be varied. Such mixtures may be used for the construction of minimum thermometers. A mixture of 10 parts ether, 6 parts ordinary methyl alcohol, and water, is transparent at low temperatures, but when heated above a certain point, which varies with the quantity of water, it becomes turbid, and resolves itself into two layers. With this liquid, therefore, maximum thermometers may be constructed (Duclaux, *Compt. rend.* lxxxii. 815).

Ebullition of Superimposed Liquids.—According to Gernez (*ibid.* lxxxvi. 472), superimposed liquids having no chemical action upon one another, boil at the

same temperature as that at which the sum of the maximum tensions of their vapours is equal to the pressure. The following are examples :

	Boiling temperature	Sum of the maximum tensions of the two vapours at the boiling temperature	Excess of pressure	Pressure
Carbon bisulphide and water . . .	43·68°	766·64	1·29	765·35
Carbon chloride and water . . .	66·17	747·36	1·91	745·45
Benzene and water . . .	69·43	765·92	1·48	764·44

On the Distillation of Liquids not miscible with Water in a Current of Steam, see Naumann, p. 948 of this Volume.

An Apparatus for Measuring the Heat of Vaporisation of Liquids is described by Berthelot (*Compt. rend.* lxxxv. 646); and an Apparatus for Measuring the Heat evolved in the Compression of Liquids, by Favre et Laurent (*Ann. Chim. Phys.* [5], i. 433).

LITHIA-PSILOMELANE and **LITHIOPHORITE**. See MANGANESE OXIDES.

LITHIUM. *Occurrence.*—This element has been found in nearly all the members of the Upper and Lower Muschelkalk in the neighbourhood of Würzburg; also in the Loess of Geisnidda in Upper Hesse, a river-deposit 20 to 30 feet thick on the edge of the Nidda Valley. The portion of this deposit which is insoluble in hydrochloric acid contains 0·007 per cent. of lithia (Hilger, *Deut. Chem. Ges. Ber.* viii. 335; *Landw.-Versuchs-Stationen*, xviii. 166).

According to Truchot (*Compt. rend.* lxxviii. 102?), the soil of Limagne in Auvergne is very rich in lithium, 100 grams of it containing from 31 to 132 milligrams of lithium carbonate. The lithium passes into nearly all the plants growing on this soil, even rape and marigolds containing it. Contrary to the statement of Grandcau (*Jahresb. f. Chem.* 1872, 234) 100 grams of the ashes of these plants were found by Truchot to contain 10 mgm. lithium chloride; 100 grams of tobacco ash yielded 440 mgm. of the same salt. Several mineral waters of Auvergne were also found to contain lithium, viz.—

Name of Water	LiCl in 1 litre	Name of Water	LiCl in 1 litre
Mont Dore	8 mg.	La Bourboule	18 mg.
Royat, source César	9	Sainte-Nectaire	22
Clermont :		Chatel-Guyon	28
Source des Salins	14	Saint-Alyre	31
Source de Jaude	15	Les Roches	33
Source de Loiselet	18	Chateaufneuf	35
Artesian Well	20	Royat, source de l'établissement	35

According to Fresenius (*J. pr. Chem.* [2], xv. 278), the warm spring of Asmannshausen in Nassau contains 0·01746 pt. per thousand of normal lithium carbonate, Li_2CO_3 .

S. de Luca (*Compt. rend.* lxxxvii. 174) has detected lithia in the trachytic earth and the water of the Solfatara at Pozzuoli.

L. Dieulafoy (*Ann. Chim. Phys.* [5], xvi. 377) has shown that lithium is much more widely diffused in nature than has hitherto been supposed. He has found it in sea-water from all parts of the globe, in quantity sufficient to be easily recognisable by the spectroscope in the residue obtained by evaporating less than a cubic centimeter of the water; in larger quantity in the water and the mud of salt marshes; in salt springs, and in mineral waters belonging to the primary rocks; further in these rocks themselves (granite, syenite, gneiss); and in gypsums both of the secondary and tertiary formations—not however in the crystals of pure calcium sulphate, but in the marls which accompany them. The general conclusion is that lithia is as widely diffused as potash and soda, and is found accompanying them in rocks of all ages, in sea water and in mineral waters.

Preparation.—The following method of preparing lithium-salts on the large scale from lepidolite, as practised at Schering's works in Berlin, is described by Filsinger (*Dingl. pol. J.* cccix. 183; cccxii. 321, 385). The finely ground and sifted mineral is stirred up to a thin paste with strong sulphuric acid in a warm brick trough, and digested, with gentle stirring till it forms into lumps, which are then calcined in a

reverberatory furnace and thoroughly lixiviated with water while still warm. The lye thus obtained is mixed with a quantity of potassium carbonate sufficient to convert all the alumina into alum; the alum-meal which separates on boiling is removed; and the small remaining quantity of alumina is precipitated by milk of lime. All the lyes are then united; the salts are converted into chlorides by precipitation with barium chloride; the liquid is evaporated to dryness; the chlorides of lithium and calcium are extracted with absolute alcohol; the alcohol is distilled off; the calcium precipitated with ammonium oxalate; any heavy metals that may be present are precipitated by a small quantity of ammonium sulphide; and the lithium chloride, which is now quite pure, is evaporated in a large silver vessel. The solution of this salt, treated with ammonia and ammonium carbonate, yields lithium carbonate in the form of a very light precipitate which may be freed from chlorides by washing with alcohol of 60 per cent. (see also Petersen, *Dingl. pol. J.* cxxiv. 176; *Jahresb. f. Chem.* 1877, 1153; *Chem. Soc. J.* xxxii. 706).

On the Spectroscopic Estimation of Lithium, see Truchot (*Compt. rend.* lxxviii. 1022) and Ballmann (*Zeitsch. anal. Chem.* 1875, 297).

Borates. Filsinger (*Arch. Pharm.* [3], viii. 198) has examined the following borates of lithium: $\text{Li}^2\text{O} \cdot 2\text{B}^2\text{O}^3 + 5\text{H}^2\text{O}$, $\text{Li}^2\text{O} \cdot 3\text{B}^2\text{O}^3 + 6\text{H}^2\text{O}$, and $\text{Li}^2\text{O} \cdot 4\text{B}^2\text{O}^3 + 10\text{H}^2\text{O}$. The first two of these salts are formed on dissolving lithium carbonate in aqueous boric acid, the former with excess of the carbonate, the latter with excess of boric acid. The third salt is produced by boiling lithium acetate with boric acid for some time, and repeatedly evaporating the solution to a syrupy consistence till all excess of acetic acid is driven off. All three are easily soluble in water, but insoluble in alcohol. The first two do not crystallise, but dry up to gummy masses, which, however crumble to granular powders after prolonged treatment with alcohol. The third salt separates, after prolonged standing, in white hard crystalline crusts.

On Sulphate and Pyrophosphates of Lithium, see the respective Acids.

LITHOFRACTEUR. See EXPLOSIVES (p. 766).

LITHOSPERMUM. The ash of the seeds of gromwell (*Lithospermum officinale*) has been analysed by L. Hornberger (*Liebig's Annalen*, clxxvi. 85). The seeds yielded 41.47 per cent. ash, which, after deduction of charcoal and CO^2 , gave in 100 parts:

CaO	MgO	K ² O	Na ² O	Fe ² O ³	SO ³	P ² O ⁵	SiO ²
59.01	3.15	6.17	0.77	0.28	0.77	2.17	27.68 = 100

LIVER. On Chemical Changes in the Liver, see C. Flüggö (*Zeitschr. f. Biologie*, xiii. 133-171; *Chem. Soc. J.* xxxiv. 160).

On the Formation of Glycogen in the Liver, and its Conversion into Glucose, see GLYCOGEN (p. 877); further, Cl. Bernhard (*Compt. rend.* lxxxii. 114, 173, 777, 1351, 1405; lxxxiii. 369, 407; lxxxiv. 1201; lxxxv. 519; *Ann. Chim. Phys.* [5], viii. 367; ix. 207; xi. 256; xii. 397; *Jahresb. f. Chem.* 1876, 922; 1877, 980; *Chem. Soc. J.* xxxiv. 82).

On the Estimation of Glycogen in the Liver, see G. Salomon (*Zeitschr. anal. Chem.* 1874, 470; *Jahresb. f. Chem.* 1874, 1051).

On Liver-ferment, see FERMENTS (p. 780).

LOLLINGITE. This mineral occurs at Mont Challanches in Dauphiné, massive, and in small crystals only $\frac{1}{2}$ mm. long, and of the form $\infty P \cdot \frac{1}{2} \bar{P} \infty$. An analysis of the massive portion gave:

Fe	Co	As	Si	S	Sp. gr.
21.22	6.44	63.66	5.61	3.66 = 100.59	6.34 at 16°

leading to the formula FeAs_2 . Measurements of the crystals by Schrauf gave, as mean values, $\infty P : \infty \bar{P} = 113^\circ 40'$; $\frac{1}{2} \bar{P} \infty : \frac{1}{2} \bar{P} \infty = 133^\circ 50'$; $\frac{1}{2} \bar{P} \infty : \infty \bar{P} = 77^\circ 25'$, whence the axial ratio is $a : b : c = 1.535 : 1 : 1.970$, which agrees nearly with that given by Dana for mispickel, viz. 1.4793 : 1 : 1.7588.

LOPHINE, $\text{C}^2\text{H}^{16}\text{N}^2$. This compound is the chief product formed by the decomposition of nitroso-amarine at 149° - 150° (p. 70). Its formation by the dry distillation of hydrobenzamide in presence of air is accompanied by evolution of light (p. 1063).

LORANTHUS. K. Martins (*N. Rep. Pharm.* xxiv. 687) finds, from examination of several branches of *Acacia Verck*, on which gummy exudations had formed, that these exudations are produced by a parasite which he designates as *Loranthus senegalensis*.

LOTUR BARK (O. Hesse, *Deut. Chem. Ges. Ber.* xi. 1542-1546). This bark, from *Symplocos racemosa*, contains three alkaloids, viz. *loturine*, 0.24 per cent.; *colloturine*,

0.02; and *loturidine*, 0.06 per cent. The alkaloïds are extracted from the bark by hot alcohol, and are converted into acetates. Loturine and colloturine are precipitated from the neutral solution by the addition of potassium thiocyanate, leaving the loturidine in solution. The crystalline precipitate is decomposed by soda, and the alkaloïds are extracted with ether and recrystallised from alcohol. The efflorescent crystals of loturine are separated mechanically from the non-efflorescent crystals of colloturine.

Loturine is soluble in alcohol, ether, chloroform, and acetone, but insoluble in water, ammonia, and caustic soda. It gives no coloration with ferric chloride, with strong sulphuric or nitric acid, or on the addition of bleaching powder and ammonia to its alcoholic solution acidulated with hydrochloric acid. Loturine melts at 234° , and sublimes, forming colourless prisms. A solution of loturine in dilute acids exhibits a fluorescence brighter than that of quinine sulphate. Loturine forms well-crystallised salts. The hydrochloride, which crystallises in white prisms soluble in alcohol and in water, forms double salts with the chlorides of platinum, gold, and mercury. The hydriodide forms a crystalline double salt with mercuric iodide. The nitrate, thiocyanate, acetate, chromate, and picrate are crystalline compounds. The tannate and phosphotungstate are amorphous powders.

Colloturine is deposited from alcohol in prisms terminating in pyramids, which sublime at 234° . The solution of the alkaloïd in dilute sulphuric or hydrochloric acid is fluorescent. Gold chloride produces a yellow amorphous precipitate in the solution of the hydrochloride.

Loturidine.—The filtrate from the thiocyanates of loturine and colloturine is rendered alkaline by ammonia, and the loturidine extracted with ether. Loturidine is a yellowish-brown amorphous body yielding amorphous salts. It dissolves in strong nitric and sulphuric acids, forming yellow solutions. The solution in dilute acids is fluorescent.

Winckler's *californine* (i. 722) was not a simple substance, but a mixture of the acetates of these three alkaloïds.

LOXOCLASE. A soda-felspar with orthoclasic cleavage, and therefore resembling Breithaupt's loxoclase (iii. 735), has been examined by Ch. Vélain (*Compt. rend.* lxxix. 250). It occurs, with augite and epidote, in the slags and tufas of the island of Rachgoun, Algeria, and, like the augite, exhibits all the signs of derivation from the older rocks by whose decomposition the tufas have been formed. The mean of three analyses gave:

SiO ²	Al ² O ³	CaO	Na ² O	K ² O	MgO	Sp. gr.
66.72	19.73	2.20	7.63	3.71	0.10 = 100.09	2.58

LUDLAMITE. A hydrated basic ferrous phosphate, found in Cornwall, associated with quartz, chalybite, vivianite, iron pyrites, and mispickel. Hardness = 3.4; sp. gr. = 3.12. Colour, clear green, from pale to dark, transparent and brilliant. Streak very pale green, approaching to white. It tinges the flame of the blowpipe slightly green, and yields a semi-fused blackish residue. It is soluble in dilute mineral acids, and is readily decomposed by boiling with a solution of caustic alkali. Analysis gave as follows:—

Fe	P ² O ⁵	H ² O
52.76	30.11	16.98 = 99.85

These numbers correspond very closely with the formula $7\text{FeO} \cdot 2\text{P}^2\text{O}^5 \cdot 9\text{H}^2\text{O}$. The mineral differs from vivianite, $(3\text{FeO} \cdot \text{P}^2\text{O}^5 \cdot 8\text{H}^2\text{O})$, in the fact that it decrepitates violently when heated, and breaks up into brilliant crystalline plates of a deep bluish-green colour. Vivianite, on the contrary, does not decrepitate, but gradually exfoliates and turns white (F. Field, *Phil. Mag.* [5], iii. 52).

Ludlamite is monoclinic, with the axial ratio $a : b : c = 0.4439 : 1 : 0.8798$. Angle $ac = 79^{\circ} 27'$. Observed faces, $\pm P$, $-\frac{1}{2}P$, ∞P , $0P$, ∞P , $+P$, $+2P$, R . Cleavage distinct parallel to $0P$. The crystals are optically positive, the optic axes lying in the plane of symmetry. Acute bisectrix = $88^{\circ} 54'$. Dispersion inconsiderable; $\rho > \nu$ (Maskelyne, *ibid.* iii. 54, 135, 525).

LUDWIGITE. This mineral, from the Banat, is parallel-fibred and mostly short-fibred. Sp. gr. = 3.907 to 4.016. Hardness = 2. Tough, difficult to split. Colour blackish-green to black. Lustre silky. Streak-powder blackish-green. Thin splinters melt with difficulty to a black magnetic slag. Dilute hydrochloric acid dissolves the powder very quickly. Its composition, according to E. Ludwig, is:

P ² O ⁵	Fe ² O ³	FeO	MgO
16.09	39.92	12.46	31.69 = 100.16
15.06	39.29	17.67	26.91 = 98.93

whence may be deduced the formula $3\text{MgO.B}^2\text{O}^3 + \text{FeO.Fe}^2\text{O}^3$, representing it as a molecular compound of normal magnesium borate and ferroso-ferrie oxide.

Ludwigite occurs in the southern part of the mining district of Morawitz, and on the western outcrop of the limestone, associated with a very compact magnetic iron-ore imbedded in the crystalline limestone, in the neighbourhood of a cleft traversing that formation. The ludwigite occurs only in isolated lumps in the magnetic iron ore, which often traverses it in thin threads (G. Tschermak, *Liebig's Annalen*, clxiv. 112).

A decomposition-product of the blackish-green variety of this mineral has been examined by F. Berwerth (*Min. Mitth.* 1874, 247). Sp. gr. = 3.41. Mineralogical examination shows that it is a mixture of brown iron-ore, talc, brucite, magnesite, and calcite, and this result is confirmed by the direct chemical analysis of the product, as appears from the following comparison:

	Fe^2O^3	CaO	MgO	CO^2	SiO^2	H^2O	B^2O^3	
Brown iron-ore	75.44	—	—	—	—	12.73	—	= 88.17
Talc	—	—	1.44	—	2.88	0.22	—	= 4.54
Brucite	—	—	3.08	—	—	1.39	—	= 4.47
Magnesite	—	—	1.40	1.54	—	—	—	= 2.94
Calcite	—	0.09	—	0.07	—	—	—	= 0.16
Totals	75.44	0.09	5.92	1.61	2.88	14.34	—	= 100.28
Direct analysis	75.34	0.09	5.80	1.65	2.83	14.51	0.80	= 101.02

LUPINE. The transformations of substance which take place during the germination of lupine-seeds have been examined by Schulze, Umlauf, a. Urich (*Deut. Chem. Ges. Ber.* ix. 1314). Out of the 45 per cent. of albuminoids (conglutin and albumin) contained in the ungerminated seeds, there remained, after fifteen days' germination in the dark, only 8 per cent., the remaining 37 per cent. having been decomposed. The chief nitrogenous decomposition-product was asparagine, besides which there were formed small quantities of other amides not isolated, and a very small quantity of ammonia. The sulphur of the decomposed albuminoids appeared to be converted into sulphuric acid, as the proportion of sulphates in the sprouts increased considerably. No separation of non-nitrogenous substances in the decomposed albuminoids was observed to take place.

LUPULINE. This name is given by Griessmayer to a base obtained by distilling the aqueous extract of hops with lime or magnesia (p. 1040).

LUTECOBALT COMPOUNDS. See COBALT-BASES (p. 546). On the crystalline form of the Chloride, vii. 365.

LUTIDINE. See PICOLINE-BASES.

LUZONITE. See ENARGITE (p. 733).

LYCINE. The base from *Lycium barbarum*, to which this name was applied by Husemann a. Marmé (iii. 738), has been shown by later researches of Husemann to be identical with botaine (p. 323).

LYCOPERDON. The substance called 'Indian Bread,' sometimes used as food by the North American Indians, consists of a parasitic fungus (*Lycoperdon solidum*) found growing in tuberose masses, weighing from an ounce to several pounds, on the roots of coniferous trees. Its surface is ash-grey and wrinkled, while the inside is nearly white and has the appearance of starch. The same substance is found in China and Japan, where it is called respectively 'Fuhling' and 'Tucka-hoe.'

The following analyses made by Braun in 1871 and by Keller in 1876 (*Chem. News*, xxiv. 168, 881) show that the composition of this fungus is subject to great variations, due, according to W. Mallet, to the penetration of the roots of the tree by the mycelium of the fungus, which converts the woody fibre of the roots into its own substance. In the specimen analysed by Braun, this process appears to have been only in its incipient stage, whereas in that analysed by Keller, it must have been nearly complete:

	Braun	Keller
Water	14.16	10.70
Glucose	0.93	0.87
Gum	2.60	2.98
Pectose	17.34	77.27
Woody Fibre	64.45	3.76
Nitrogen in insoluble combination	0.36	—
Proteids	—	0.78
Mineral substances:		
Soluble in Water }		
Insoluble in Water }	0.16	{ 0.08
		{ 3.56

The ash analysed by Keller was found to contain :

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	Cl	SiO ₂	
4.675	2.192	5.169	11.375	11.808	19.781	1.587	1.642	41.771	= 100.000
Deduct O for Cl									0.370
									99.63

LYCOPODIUM. The following analyses of club-mosses are by G. W. Hawes (*Sill. Am. J.* [3], vii. 585):

	C	H	O	N	Ash
<i>Lycopodium dendroideum</i>	47.11	6.39	41.85	1.40	3.25 p. c.
"	47.29	6.43	41.62	1.38	3.28 "
" <i>complanatum</i>	45.78	6.25	40.66	1.84	5.47 "
"	45.62	6.26	40.79	1.84	5.49 "

M

MACLURIN, MORIN, and MORINTANNIC ACID. These three constituents of fustic have been examined by J. Löwe (*Zeitschr. anal. Chem.* 1875, 117). They contain a common nucleus with 15 at. carbon. The amount of water in crystallised morin differs accordingly as it is crystallised from hot water or from alcohol. Löwe's analyses lead to the following formulæ:

Morin dried at 100°	C ¹⁵ H ¹⁰ O ⁷
" precipitated by water from alcoholic solution	C ¹⁵ H ¹⁰ O ⁷ + H ² O
" recrystallised from water	C ¹⁵ H ¹⁰ O ⁷ + 2H ² O
Egg-yellow Lead-compound of Morin	C ¹⁵ H ¹² O ⁸ + PbO
Orange-yellow "	C ¹⁵ H ¹⁰ O ⁷ .2PbO

Maclurin dried over sulphuric acid has the composition C¹⁵H¹²O⁸; it gives off water at 120°–130°, leaving C¹⁵H¹⁰O⁷. Its alcoholic solution yields with lead acetate a precipitate having the composition C¹⁵H¹⁰O⁷.3PbO. Aqueous solutions of maclurin are precipitated by alkaloids, gelatin-solution, and albumin.

Morintannic acid, C¹⁵H¹²O⁷, forms a lead compound having the composition 2C¹⁵H¹²O⁷.5PbO. It differs from maclurin by containing 1 at. oxygen less.

MACONITE. A mineral from Macon County, North Carolina, where it is found accompanying corundum (p. 570).

MACROCHORDION. See BROMELIACEÆ (p. 350).

MAGNESIA-MICA. See MICA.

MAGNESITE. The crystallised magnesites of the north-eastern Alps have been examined by J. Rumpf (*Jahrb. f. Min.* 1874, 540).

1. Beautiful small crystals of this mineral occur at Mariazell, in Styria. They exhibit the combination $OR \propto P2$, have a length of 1.6 mm., and are sometimes transparent and colourless, more often yellowish-brown. Sp. gr. = 3.038. Analysed by Rumpf.

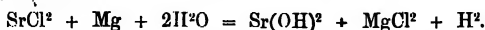
2. A second locality is an iron mine near Flachau, in Salzburg. Light grey crystals, likewise exhibiting the combination $OR \propto P2$. Sp. gr. = 3.015. Analysed by K. Sommers.

3. Remarkable is the occurrence of lenticular magnesite crystals in the block-shaped masses of magnesite lying between clay-slates. These crystals are known in Styria by the name of pinestone (*Pinolistein*, probably from the resemblance of their section to that of the fruit of *Pinus pinea*). Rumpf proposes to designate the magnesite rock as *Pinolite*. It consists mainly of crystalline milk-white magnesite and clay-slate, which, however, is in some parts replaced by talc-slate. The magnesite crystals have the appearance of flat lentils abundantly disseminated through the clay-slate in variously shaped bundles and tufts. The principal localities are the mountain-gorge of the Sund (a) and Wald (b), in Styria, and the Semmering in Lower Austria. Analyses of magnesites from the two first-named localities have been made by Fr. Ullik.

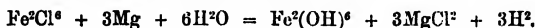
	MgO	CaO	Fe ₂ O ₃	FeO	MnO	CO ₂	H ₂ O	Insoluble
(1)	45.32	1.58	—	2.12	—	50.90	0.36	0.34 = 100.62
(2)	44.53	0.65	3.62	—	0.28	49.67	0.61	0.58 = 99.94
(3, a)	45.60	1.01	—	1.74	—	51.87	—	0.25 = 100.47
(3, b)	45.55	0.86	—	1.62	—	51.62	—	0.47 = 100.12

MAGNESIUM. Experiments on the action of metallic magnesium on various metallic salts have been made by S. Kern (*Chem. News*, xxxii. 309; xxxiii. 112, 236). Concentrated solutions were used and left in contact with magnesium ribbon for 30–40 hours. The experiments show that most metallic salts are converted by the action of magnesium into oxides or hydroxides.

Cobalt chloride is decomposed, with evolution of hydrogen and deposition of a green substance containing cobalt oxide. With *silver nitrate* a precipitate of silver oxide is obtained. In a solution of *lead nitrate*, the magnesium quickly becomes covered with metallic lead in the form of a very fine powder, which is soon converted into Pb(OH)^2 . *Strontium salts* require much more time to decompose them. Concentrated strontium chloride solution, in contact with magnesium for two days, gives a white precipitate of strontium hydroxide:



Mercuric chloride with magnesium gives a greyish precipitate, which turns red when ignited. This precipitate is a third form of mercuric oxide, which had hitherto been known only as a red or yellow precipitate. *Platinic chloride* with magnesium evolves hydrogen. After about 20–25 hours a black precipitate of metallic platinum is formed. On leaving it in contact with water, brown Pt(OH)^4 is obtained. *Ferric chloride* is rapidly converted into ferric hydrate:



With *zinc salts* magnesium eliminates hydrogen very slowly; with zinc chloride after 48 hours a small amount of hydroxide was formed. In a solution of *sodium chloride* magnesium also eliminates hydrogen very slowly, sodium hydroxide being formed, which quickly turns red-litmus paper blue. *Manganous chloride* yields manganous oxide, rapidly oxidised to manganoso-manganic oxide, Mn^2O^4 . *Uranic nitrate* yields uranic oxide. *Potassium dichromate* is but slowly attacked, with formation of magnesium dichromate and potassium hydroxide. *Aluminium salts* are very slowly attacked, with formation of aluminium hydroxide. From a *palladium solution* magnesium eliminates hydrogen, forming palladium monoxide, together with a small quantity of metallic palladium which unites with the hydrogen, forming Pd^2H . In a solution of *copper*, the magnesium quickly becomes coated with metallic copper. A solution of *sal-ammoniac* is decomposed by magnesium, with rapid evolution of hydrogen.

Detection and Estimation.—A delicate spectroscopic reaction for magnesia and for alumina is afforded by the absorption-spectrum of a solution of purpurin mixed with one or other of these bodies. A dilute aqueous solution of pure purpurin shows a weak absorption in the yellow, and a stronger in the green, between F and b. This absorption becomes more intense when ammonia is added, and disappears on adding dilute acetic acid, a faint absorption in the blue alone remaining. But when to a very dilute aqueous solution of purpurin a dilute solution of alum is added, the liquid becomes red, and gives two strong absorption bands between D and E and b and F. This reaction, which is also produced by other aluminium salts, is best seen in a very weak alkaline solution; it is weakened but not destroyed by acetic acid.

Magnesium salts give the same bands, only that in the yellow is stronger than the other, but the least excess of acetic acid destroys the spectrum. The least traces of magnesium and aluminium can be detected by this reaction, which is not shown by the salts of iron, manganese, zinc the alkali-metals, or those of the alkaline earths; it does not appear when salts of iron or zinc are present in excess (H. W. Vogel, *Deut. Chem. Ges. Ber.* ix. 1641).

For the precipitation of magnesia as ammonio-magnesium phosphate, C. Mohr (*Zeitschr. anal. Chem.* 1873, 36) recommends the use of ammonio-sodium phosphate, by which the magnesium is thrown down at once as crystalline ammonio-magnesium phosphate. The same method is recommended by W. Gibbs (*Chem. News*, xxviii. 51) with the addition that the precipitation with phosphorus-salt should be performed in a hot concentrated solution, and ammonia added only after cooling.

On the estimation of magnesia in a mixture of alkaline and earthy sulphates, see SULPHATES.

Separation from Calcium.—Sonstadt (*Chem. News*, xxix. 209) employs for this purpose a concentrated solution of *potassium iodate*, which throws down the calcium as iodate without perceptibly redissolving it, but does not precipitate magnesium salts, and has the further advantage of not interfering with the subsequent precipitation of the magnesium by ammonio-sodium phosphate, the resulting precipitate of ammonio-magnesium phosphate being, on the other hand, less soluble in the liquid containing the calcium iodate, than in dilute ammonia. Sonstadt regards this method of separation as much more effective than the ordinary method with ammonium

oxalate, inasmuch as when the latter is employed, not only is a small portion of magnesia thrown down with the lime, but the presence of the magnesium salts likewise interferes with the complete precipitation of the calcium as oxalate.

Magnesium chloride. A hydrated chloride of magnesium, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, named *Bischofite*, is found, together with carnallite, in cavities and as a crust on rock-salt in the Stassfurth mines. The crystals of bischofite often contain microscopic crystals of sodium chloride, and may be distinguished from carnallite by the fact that they are very deliquescent, harden on exposure to a temperature of 40° – 45° , but deliquesce when the temperature falls: this property is not possessed by carnallite. They are transparent or white and more or less opaque. Hardness 1.7. Sp. gr. 1.65. When heated, they give off water and hydrochloric acid, and leave a residue of oxychloride.

Oxychloride.—Bender, by mixing calcined magnesia with a strong solution of magnesium chloride, and leaving it exposed to the air for six months, obtained a pasty mass which he regarded as a mixture of the oxychloride, $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 17\text{H}_2\text{O}$, with normal magnesium carbonate (vii. 759). It is, however, by no means certain that magnesia is completely converted into normal carbonate by exposure to the air, and moreover, an oxychloride differing in composition from Bender's salt is obtained by mixing freshly calcined magnesia (30 grams) with solution of magnesium chloride (1500 grams) in a flask well corked and nearly filled with the mixture, and heating it in a water-bath, with frequent agitation, till the liquid when examined under the microscope exhibits nothing but needle-shaped crystals. These crystals, when washed with water, and dried at 110° , were found to consist of $\text{MgCl}_2 \cdot 10\text{MgO} + 14\text{H}_2\text{O}$, and when dried over soda, of $\text{MgCl}_2 \cdot 10\text{MgO} + 18\text{H}_2\text{O}$. When dry they withstand the action of carbonic acid, but are completely decomposed by it when moist. The pasty mass obtained by kneading magnesia with solution of magnesium chloride, is a mixture of the 18 mol. hydrate with basic magnesium carbonate (O. Krause, *Liebig's Annalen*, clxv. 38).

Nitride, Mg_2N_2 . Briegleb a. Geuther obtained this compound as a greenish-yellow amorphous mass by passing ammonia or nitrogen gas over strongly heated magnesium (iii. 754); and J. W. Mallet (*Chem. News*, xxxviii. 39) has lately observed the formation of the same substance in large quantity by the simple combustion of magnesium with limited access of air. The chief part of the metal burned is, of course, converted into oxide, and the temperature produced by the combustion is high enough to induce the remainder, when the supply of oxygen is limited, to unite with nitrogen.

The following three experiments show the largest absorption of nitrogen:

	Mg. used grms.	Nit ⁿ obtained grms.	Equiv. Mg_2N_2 grms.	Equiv. Mg. grms.	Mg. converted into nitride per 100 pts. used
No. 1 . . .	2.635	0.292	0.859	0.618	23.5
No. 2 . . .	2.204	0.286	0.841	0.606	27.5
No. 3 . . .	3.117	0.365	0.773	0.773	24.8

Aluminate, $\text{MgO} \cdot \text{Al}_2\text{O}_3$. This compound may be obtained in the crystalline state by packing 25.5 grams of pure and freshly ignited magnesia in a crucible of hard carbon, imbedding in the centre a lump of aluminium containing 8 grams of the pure metal, and raising the whole to a very high temperature. After cooling, the whole of the aluminium, the magnesia, and the crucible were separately treated with moderately strong, hot, hydrochloric acid, and the solutions filtered. The greyish residue left on the filters from the first two solutions was dried, ignited in a stream of oxygen to burn off some specks of carbon, and on being examined with the microscope was found to consist of minute, colourless, transparent crystals of two kinds: the one being thin elongated scales, consisting of pure alumina; the other of regular octahedrons, which scratched glass readily, and on fusion with acid sodium sulphate yielded magnesia 28.99 per cent., and alumina 70.81 per cent., giving the ratio, $\text{MgO} : \text{Al}_2\text{O}_3 = 725 : 689$, and showing that these crystals consisted of artificial spinelle, MgAl_2O_4 .

Magnesium-alum, $\text{MgAl}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ (v. 583), has been found in lamino-crystalline masses, and occasionally in long-fibred bundles, on the island of Negros, Philippine group. When recrystallised it formed small crystals exhibiting the combination $\text{O} \cdot \infty \text{O} \cdot \infty$. Analysis gave:

SO_4	Al_2O_3	MgO	CaO	H_2O
37.76	12.60	3.52	0.91	45.21 = 100

(Frenzel, *Min. Mitth.* 1877, 303).

MAGNETIC IRON ORE. MAGNETITE. This mineral, occurring with amethyst veins in the trapp of Annapolis County, Nova Scotia, has been analysed by H. How (*Phil. Mag.* [5], i. 136).

Quartz	MgO ⁽¹⁾	O ⁽²⁾	Fe
5.46	1.27	24.94	68.33 = 100
4.94	4.84	25.19	65.03 = 100

(¹) With traces of CaO.

(²) Determined by difference.

J. Strüver (*Zeitschr. f. Kryst.* i. 230) has described the magnetite of the Alban mountains (ancient Iatium), where it occurs, partly as a constituent of the lavas, partly in goodes, partly in loose crystals in ashes and tufas, and in the sands of streams and lakos. The forms observed were 0, $\infty 0 \infty$, $\infty 0$, 202, 303, $\infty 03$, 50 $\frac{5}{2}$, of which the fourth and sixth are new for magnetic iron oxide. Older authorities assign to the magnetic iron ore of this locality a very large amount of titanium; Struve however found only traces.

Fine crystals of magnetite are found at Mulatto, implanted on a solid mass of the mineral and exhibiting the faces $\infty 0$, 50 $\frac{5}{2}$, 303, 0 (Doelter, *Jahrb. f. Min.* 1877, 647).

A. Knop (*Zeitschr. f. Kryst.* i. 64) has analysed a titaniferous magnetic iron oxide from oncllosures in the Sanidin-Hayn-Phonolite from Horberig near Oberbergen in the Kaiserstuhl range, with the following results:

Fe ² O ³	TiO ²	Al ² O ³	MgO	MnO
88.41	4.08	6.85	4.57	trace = 103.91

These values correspond with the following:

Fe ² O ³	Fe(Fe, Ti) ² O ³	MgAl ² O ³	MgFe ² O ³
69.84	11.42	9.54	9.40 = 100.20

J. R. Müller (*Zeitschr. f. Kryst.* i. 512) has analysed the magnetic iron ore from the Kaschberg in Bohemia, consisting of mixtures of augite and magnetite, which latter can be very accurately separated by the magnet:

Fe ² O ³	AlPO ³	FeO	CaO	SiO ²
61.14	0.4815	32.2164	3.507	1.0655 = 98.4104

Magnetic iron sand has lately been found in a granite vein accompanied by an excess of mica, at Grotta d'oggi, near San Piero, Elba. The upper part of the magnetic iron deposit is partially decomposed, and contains numerous black magnetite crystals some of which exhibit a bronze-like tarnish. The crystals, which are octahedrons or rhombic dodecahedrons, or combinations of the two, have a diameter of from $\frac{1}{2}$ to 1 centimeter, and are strongly polar-magnetic. Lower down in the vein-stone the magnetite crystals increase in size, but are less freely crystallised. Magnetite also occurs in the green diorite slate, at Caviere, near San Piero, but it is not so strongly magnetic as that found in the granite, and not crystallised (G. Roster, *Jahrb. f. Min.* 1877, 531).

Allotropic Varieties of Magnetic Iron Oxide.—This oxide, when obtained by heating ferric oxide for some hours in hydrogen gas or carbonic oxide at 350°–440°, or by heating the hydrate of the magnetic oxide at 300° in an indifferent gas, or by calcining pyrophoric ferrous oxide at a low red heat, passes into ferric oxide by calcination in the air, and is attacked by concentrated nitric acid. Its density is 4.86. Magnetic oxide obtained at a high temperature by burning iron in oxygen, or by decomposing the sesquioxide at a bright red heat, has a density of 5 to 5.09, and does not possess those properties. Pyrophoric ferrous oxide is transformed when heated in the air into ferric oxide, but if this substance be heated to dull redness in carbonic acid gas, magnetic oxide is obtained identical with the first variety mentioned above. If this variety be heated intensely in nitrogen, the second kind, namely, that which is incapable of taking up more oxygen, is obtained (H. Moissan, *Compt. rend.* lxxxvi. 600).

MAGNETIC PYBITES. The following are recent analyses of this mineral:

- (1). From Elizabeth Town, Canada, by J. Lawrence Smith (*Compt. rend.* lxxxi. 976).
- (2). From the same locality, by Lindström (*Deut. Chem. Ges. Ber.* ix. 858).
- (3). From Todtmoos in the Schwarzwald, by A. Hilger (*Liebig's Annalen*, clxxxv. 208):

Fe	Cu	Mn	Ni	Co	S	SiO ²	X	Sp. gr.
59.88	—	—	—	—	39.24	—	1.01 = 100.13	4.642
60.56	0.145	0.06	0.112	0.111	39.02	0.036	— = 100.044	4.622
56.58	0.54	—	1.82	0.48	40.46	—	— = 99.88	4.12–4.2

The proportions of iron and sulphur in these analyses agree most nearly with the

formula Fe_7S_8 , which requires 60.5 Fe and 39.5 S. The formula FeS requires 63.6 Fe and 36.4 S.

The crystals from Elizabeth Town are composite, three individuals of the combination 2^0P . 0P , being grown together in the direction of the faces of the pyramid P , whereby the axes of the individual crystals are set perpendicularly to each other (E. S. Dana, *Sill. Am. J.* [3], xi. 386). Crystallised magnetic pyrites from Bottino in Italy exhibits the faces P (?), 0P , ∞P , 2P , 6P (Grattarola a. d'Achardi, *Zeitschr. f. Krystallographie*, i. 526).

MAGNETISM. *Relationship of the Magnetic Metals.*—The following table, exhibiting the physical resemblances between the magnetic metals, iron, cobalt, and nickel, has been drawn up by W. F. Barrett (*Phil. Mag.* [4], xlv. 478):

Substance	Density	Atomic weight	Specific heat	Atomic heat	Dilatation		Conductivity	
					By heat	By strain	For heat	For sound
Iron . .	7.8	56.0	0.1138	6.38	.0926	.0387	.168	15.3
Nickel . .	8.3	58.5	0.1091	6.33	.0899	.0394	.131	14.9
Cobalt . .	8.5	58.5	0.1070	6.26	.0981	.0456	.172	14.2

These metals likewise present a remarkable similarity in many of their chemical properties. Both iron and nickel become passive when immersed in strong nitric acid; the action of the concentrated acid upon cobalt may with great probability be attributed to the of iron which it invariably contains.

Ferrous salts are bluish-green; nickel-salts emerald-green; cobalt-salts (when warmed) bright green; the change of cobalt-salts by heat may perhaps be related to the increase in the magnetic power of the metal, which likewise takes place when it is heated. Cobalt and nickel, moreover, generally occur together, and all the three metals are associated in meteoric iron. The feebly magnetic metals, manganese and chromium, likewise participate to a certain extent in the chemical properties of iron, nickel, and cobalt.

Nickel and cobalt, when magnetised by an electric current, give out, on the closing of the circuit, a sound, which in the case of cobalt is louder than with nickel, and has the metallic ring of that produced by iron under similar circumstances. Bars of iron and cobalt appear to be somewhat elongated by magnetisation; nickel does not. The result obtained with cobalt is, however, scarcely decisive, as the metal used was not quite free from iron (Barrett, *Phil. Mag.* [4], xlvii. 51).

On the effect of Magnetisation in the Physical Properties of Iron, see further p. 1096.

W. Hankel (*Ann. Phys. Chem.* [2], i. 285) has determined the magnetism of very pure nickel and cobalt, under the influence of currents of various strength. In nickel, the magnetism excited by comparatively feeble currents is nearly equal to that of iron, and differs from that of the latter in increasing ratio as the currents become stronger. Cobalt, on the other hand, acquires under the influence of weak currents only about half the magnetism of iron, and with stronger currents a fraction of that of iron becoming continually smaller as the strength of the current is greater.

H. A. Rowland (*Phil. Mag.* [4], xlv. 10; xlviii. 321) has also made comparative experiments on the behaviour of iron, nickel, and cobalt under the influence of magnetising forces, from which he infers that the differences between the magnetic characters of the three metals are only quantitative, and may be summed up in the following propositions: (1). As the magnetising force increases, the resistance to magnetisation diminishes down to a certain minimum, after which it increases without limit. (2). In nickel and cobalt this resistance depends upon the temperature, and in cobalt it diminishes with rise of temperature; in nickel it diminishes or increases with rise of temperature accordingly as the magnetising force is weak or strong. (3). All the three metals have a maximum of magnetisability, which, however, is attainable only under the influence of magnetising forces not practically available (the limit would be first attained with nickel). (4). In iron and nickel, this maximum diminishes as the temperature rises, at least between 10° and 220° , slowly in iron, quickly in nickel.

The following conclusions are deduced by A. L. Holz (*Pogg. Ann.* cli. 69; cli. 67) from experiments on the effect of solvents on steel magnets: (1). The magnitude of the magnetic moment of a steel bar depends upon the structure of the iron and that of the iron carbide associated with it. (2). This moment (referred to 1 mg. as unit of weight) is diminished by removal of magnetised iron, but increased by removal of

magnetised iron carbide. (3). The particles of iron carbide which remain after the pure iron has been dissolved out, are magnetisable and become permanently magnetic. (4). The coercive power of steel magnets and of magnets formed of electrolytically deposited iron is dependent on the distances between the molecules, the magnetic moment being increased by every process which widens these distances (see further, *Ann. Phys. Ergänzbd.* viii. 353; *Jahresh. f. Chem.* 1877, 171). L. Kalp (*Pogg. Ann.* clv. 320) concludes, from experiments on two iron bars of equal size and weight, the one having a fibrous, the other a granular texture, that the magnetic moments induced in the two by currents of equal strength are almost exactly equal, and hence infers that texture has no influence on magnetism.

From experiments by Trève a. Durassier (*Compt. rend.* lxxx. 799; lxxxi. 1123, 1246; remarks thereon by Jamin, *ibid.* lxxxi. 1126) it appears: (1). That the magnetism of very carefully prepared homogeneous steel bars penetrates them uniformly to the very centre (thickness 16 mm.), as shown by the fact that when the magnet is dissolved, its magnetism decreases proportionally to the weight. (2). That the magnetic moment decreases with the proportion of carbon, and is greater the higher the temperature of the water in which the steel has been hardened; at equal temperatures, on the other hand, it is greater with water than with oil as the refrigerating agent.

Electrolytically-prepared Magnets.—According to experiments by M. v. Jacobi (*N. Petersb. Acad. Bzw.* xviii. 11), it appears that iron electrolytically precipitated under the influence of a strong electromagnet spiral does not differ in its physical or chemical properties from iron similarly precipitated without such electromagnet influence; and in particular it does not exhibit more decided magnetic properties. Electrolytically precipitated iron shows very little coercive force, which, moreover, cannot be imparted to it even when it has been brought, by ignition and slow cooling, to the degree of softness and tenacity of bar iron, or finally converted into steel having the hardness of glass. It is capable of acquiring strong temporary magnetism, which, however, disappears very quickly.

According to W. Beetz, on the other hand (*Pogg. Ann.* clii. 484), iron electrolytically precipitated from a solution containing sal-ammoniac is capable of acquiring very strong permanent magnetism; iron similarly precipitated from other solutions possesses this power only in a minor degree. If the precipitation takes place under the influence of strong magnetism, the solution containing sal-ammoniac yields strong magnets of uniform texture, whereas a solution not containing sal-ammoniac yields magnets of irregular structure and exhibiting consecutive points, whereby the already weak magnetism of the precipitate thrown down from such solutions is made to appear still less. Under no circumstances, however, does electrolytically precipitated iron possess much coercive power, unless its structure has been altered by ignition or other processes.

Influence of Hardening and Heating on Magnetisation.—According to Gauguin (*Compt. rend.* lxxxii. 144), the hardest steel bars acquire, under the influence of powerful magnetising forces, a stronger magnetism than those which have been tempered, whereas, under the influence of a weaker inducing force, the softer steels are more highly magnetised than those of greater hardness. The magnetism of any cross section of the bar consists of an inherent portion which remains in it even after separation from the bar, and another portion due to the action of the other sections. Hardening increases the coercive power, and, therefore, also the inherent magnetism, but diminishes the temporary magnetism or magnetism of reaction. The latter, therefore, plays a more conspicuous part in steel of inferior hardness.

Jamin (*Compt. rend.* lxxvii. 89) finds that different kinds of steel form weaker electromagnets in proportion as they are harder and richer in carbon. Steel of the hardness of glass is almost unmagnetisable, and therefore not well adapted for making permanent magnets; the best steels for this purpose are those of medium hardness. When steel is re-tempered, the power of acquiring temporary magnetism increases with the degree of heat at which the tempering takes place. In steels containing a small or a medium proportion of carbon the power of acquiring permanent magnetism is greatest when they are completely hardened, is diminished by tempering, and disappears altogether at a full red heat. In glass-hard, highly carbonised steel, the latter power is increased by tempering up to a certain temperature, higher as the hardness is greater, then again diminishes, but does not disappear completely even at a full red heat.

When a bar of highly carbonised steel was removed from a sand-bath in which it had been tempered to the dark-blue, and quickly introduced into an electric spiral, its temporary magnetism (that which it possessed while still within the spiral) was found to be slightly less than that which it would have acquired in the cooled state, but its

permanent magnetism was considerably greater. At the first moment the latter appeared to be equal to the temporary magnetism, but it quickly diminished and disappeared completely in a quarter of an hour, whether the original temperature were maintained or the bar left to cool gradually. The disappearance of magnetism is exactly analogous to cooling. If the bar be again heated, but to a lower temperature, the temporary magnetism rises to a higher degree than before, sinks for a moment much lower on the breaking of the current, and then decreases more slowly than before down to a certain limit, but does not disappear altogether. On repeating the experiment upon the cold bar, a still higher temporary magnetism is developed, and a permanent magnetism greater than the residual magnetism in the preceding case.

Experiments on the influence of heat on magnetisation have also been made by Favé (*Compt. rend.* lxxxii. 276), who finds that when heated steel bars are magnetised by the electric current, the amount of permanent magnetism slowly diminishes as the temperature at which the magnetisation takes place is raised; it is still considerable at a dull red heat, but becomes imperceptible at cherry-redness. The magnetism, which disappears very quickly as the bar cools, may be retained for an indefinite time at any temperature, provided this temperature be kept constant, but every rise or fall of temperature is attended with loss of magnetic power. The quantity of magnetism retained at any particular temperature depends upon the nature of the steel, the temperature at which the magnetisation originally took place, and the changes of state which have occurred since the magnetisation. On heating the bars, the magnetism diminishes regularly according to a law depending on the composition of the steel. As the bar cools, the magnetism diminishes according to a law which (contrary to Jamin's statement) is very different from the law of cooling, the diminution being very slow at first, but afterwards taking place with increasing rapidity. The higher the temperature at which the bar was magnetised, the longer is the duration of the earlier stage of slow decrease. When a cooling bar is reheated, the magnetism again increases considerably under certain circumstances, but never regains its original value.

Dubrée (*Compt. rend.* lxxxii. 279) suggests that the results of Favé's experiments may have been somewhat influenced by the inducing action of the earth, and refers to some experiments of his own (*ibid.* lxxx. 526), in which bars formed of an alloy of platinum with 14 to 16 per cent. iron, and cast with the axis of the mould in the direction of the magnetic dip, exhibited strong magnetic polarity, which was reversed by turning the bars upside down and again heating them strongly.

The influence of heat on magnetisation has also been studied by J. M. Gaugain (*Compt. rend.* lxxx. 297; lxxxii. 685, 1422; lxxxiii. 661, 896; lxxxv. 219), whose mode of operating is similar to that adopted by Favé, excepting that the inducing power was furnished by a permanent magnet, one pole of which was placed in contact with the steel bar under investigation, and that the inducing power was in most cases made to act constantly during all changes of temperature. These experiments showed that when a bar is moderately heated, the total magnetism (permanent + temporary) is considerably increased, but that when the heat is raised till the steel turns blue, its magnetism attains a maximum value at a certain temperature depending on the nature of the steel, and then diminishes to a certain extent. When the bar is left to cool in uninterrupted contact with the inducing magnetic pole, its magnetism increases, and remains, after complete cooling, considerably higher than it was before heating, and higher in proportion as the heat was greater. A short time after the removal of the inducing magnet, part of the excess of magnetism developed by heating disappears, and cannot be restored by renewed contact with the magnet. The ratio of the difference of the two values to the higher limiting value is called by Gaugain the *transient variation*. It is very different for different kinds of steel, and greater for the several transverse sections in proportion as they are farther removed from the inducing pole. The *permanent variation* is the ratio of the difference between the magnetism of a point after heating, and that of the same point before heating, referred to a certain temperature; this variation increases with the magnetising force. In iron these two variations are smaller than in steel. Determinations of the total magnetism at different high and constant temperatures, show that in bars of great transient variation the total magnetism is weaker at 300° than at ordinary temperatures, but that in bars which exhibit only a small transient variation, the total magnetism is strongest at 300°. Sheffield steel, magnetised at a red heat, not only lost its magnetism completely on cooling, but acquired opposite polarity. On reheating, this reversed magnetism disappeared and the original polarity was restored.

New Method of Magnetisation.—When steam of 5 or 6 atm. pressure is passed through a copper tube 2 or 3 mm. thick coiled round an iron cylinder, the iron becomes magnetic, and remains so as long as the stream of vapour is kept up (D. Tommasi, *Compt. rend.* lxxx. 1007). Maumené (*ibid.* 1138) attributes this result to a thermoelectric current due to the difference of temperature between the heated inner surface and the cold outer surface of the tube.

Influence of Traction on Magnetisation.—Experiments on the effect of tractile forces on the magnetisability of wires have been made by Sir William Thomson (*Proc. Roy. Soc.* xxiii. 445, 473). Pianoforte-wire suspended vertically within an induction-spiral, and stretched by weights, acquires weaker magnetism both temporary and permanent, than when it is not stretched, the difference being more considerable for the permanent than for the temporarily induced magnetism. The variation in the magnetism consequent on repeated closing and opening of the inducing-current is greater with stretched than with unstretched wire. In wires of perfectly soft iron, the result depends on the strength of the magnetising force. When this force has attained a certain magnitude, the induced magnetism is increased by tension; but beyond that critical point it is diminished by tension. The alteration produced by repeated opening and closing of the circuit in soft iron wires is always diminished by tension, contrary to that which takes place in steel wires.

Magnetism of Chemical Compounds. Elaborate experiments on the magnetic behaviour of the salts of iron, cobalt, nickel, manganese, chromium, cerium, and didymium, have been made by G. Wiedemann (*Pogg. Ann.* cxxvi. 1; cxxxv. 177; *J. pr. Chem.* [2], ix. 145; *Phil. Mag.* [4], xxx. 366; xxxvii. 314; [5], iv. 161, 276). The apparatus used consisted of a brass bar suspended by a torsion wire of German silver, and carrying—besides a horizontal mirror for reading off the angle of rotation—a brass arm directed from north to south, on which was fixed a small glass flask filled with the substance under examination; in front of this flask was placed an electromagnet having its axis directed from east to west. This apparatus affords the means of determining the magnitude of the temporary magnetic moment of the salt under the influence of the electromagnet, previous observation having shown that the magnetic attraction is proportional to the square of the magnetic moment of the attracting electromagnet, and consequently that the temporary magnetic moment of the glass vessel filled with the solid or dissolved salt is directly proportional to the magnetic force. By subtracting from the magnetic moment which the glass vessel filled with solutions of a salt in various solvents and of various degrees of concentration exhibits under the influence of the unit of magnetic force, the magnetic moment of the same vessel filled with the pure solvent and under the influence of the same force,—and applying this method to various salts, and at various temperatures, the following results were obtained: (1). The magnetic moment of any salt dissolved in various solvents is directly proportional to the weight of that salt contained in a unit-volume of the solution, and independent of the nature of the solvent. (2). It decreases with rise of temperature, and in the same ratio for all the salts examined.

Denoting the temperature by t , the temporary magnetic moment at 0° by m_0 , and the same at t° by m_t , we have:

$$m_t = m_0(1 - 0.00395 t).$$

It is remarkable that the decrease of the magnetic moment does not differ much from the decrease of the electric conductivity of the metal for the same changes of temperature.

In the following tables, m denotes the specific magnetism of the salts according to Wiedemann's definition, that is to say the quotient of the magnetic moment developed in them by the unit of magnetising force, divided by the weight of the salt contained in a unit of volume; μ the values obtained by multiplying m into the molecular weight of the salt.

A. Estimations with Solutions.—(All data, with exception of ammonioferrous sulphate, relate to the anhydrous salt. For the mean values deduced from the results of several experiments, the number of the experiments is given in brackets).

	m	μ		m	μ
NiSO ⁴	18.40	1426	MnSO ⁴	62.18	4695
NiN ² O ⁶	15.67	1433	MnN ² O ⁶	52.46	4693
NiCl ²	21.54	1400	MnC ² H ⁴ O ⁴	53.03	4586
			MnCl ² [2]	74.74	4706
CoSO ⁴	41.52	3218			
CoN ² O ⁶	33.98	3109	Cr ² (SO ⁴) ³ [2]	19.40	3812
CoCl ²	47.08	3058	Cr ² (N ² O ⁶) ³ [3]	15.46	3705
			Cr ² Cl ⁶	25.15	3988
FeSO ⁴ [3]	51.35	3904			
FeN ² O ⁶ [2]	42.91	3861	Fe ² (SO ⁴) ³	46.48	9296
FeCl ²	60.78	3858	Fe ² (N ² O ⁶) ³	38.89	9410
FeSO ⁴ .(NH ⁴) ² SO ⁴ + 6H ² O	19.35	3795	FeCl ³	59.34	9633

B. *Estimations with Solid Salts.*—(These were introduced into the flask in the state of fine powder, and intimately mixed with ignited silica or dry potassium chloride. Here also the numbers—except in the case of ammonioferrous sulphate, refer to the anhydrous salt):

	<i>m</i>	μ		<i>m</i>	μ
FeSO ⁴ + 7H ² O . . .	46.87	3683	MnSO ⁴ cryst. . . .	60.92	4600
FeCl ²	57.71	3660	CoSO ⁴	38.09	2950
FeSO ⁴ .(NH ⁴) ² SO ⁴ + 6H ² O	20.81	4078	CoSO ⁴ [2]	38.66	2996
			Fe ² Cl ⁶	55.41	9000

These numbers show (3): that in analogously constituted salts of the same metal the product of the specific magnetism of the salt into its molecular weight is constant; or, in other words, the molecular magnetism of analogously constituted salts, including the haloïd salts, of the same metal, is a constant quantity. The mean magnetic moments of a molecule of the nickel, cobalt, ferrous, and manganoous salts are to one another as 142 : 313 : 387 : 468. The magnetism of a molecule of the cobalt-salts is nearly the mean of the magnetisms of the nickel and manganoous salts; that of the ferrous salts is intermediate between those of the cobaltous and manganoous salts. The several oxides of the same metal, FeO and Fe²O³ for example, possess different magnetic powers, and for the same oxide the magnetism varies with the form: thus it is smaller in the soluble form of ferric oxide obtained by dialysis, and in that which exists in basic salts, than in the crystalline oxide, or in that which exists in the acid salts. (4). The magnetism of salts in the solid state is nearly the same as that of their solutions; moreover the magnetism of anhydrous salts is not essentially altered by the entrance of water of crystallisation. The insoluble salts of the metals above mentioned—so far as they are not decomposed by washing with hot water—agree with the soluble salts in respect of the value of μ . From the preceding results, Wiedemann considers it probable that in all similarly constituted salts of a metal the atom of the metal, when subjected to the action of equal magnetising forces, acquires the same degree of temporary magnetism.

In a second series of experiments (*Pogg. Ann.* cxxxv. 177; *Phil. Mag.* [4], xxxvii. 314) Wiedemann shows: (5). That equality of molecular magnetism exists also in the salts of cerium, didymium, and copper. (6). The hydroxides of the magnetic metals above mentioned likewise possess nearly equal magnetism. (7). The molecular magnetism of the magnetic metals and of the atomic groups containing them, remains constant in the passage of a binary compound into another similarly constituted compound by double decomposition, so that the molecular magnetism of binary compounds may be calculated from that of their constituents in their existing state by simple addition. (8). In the double cyanides of the magnetic metals the magnetism of the atom of metal united with the cyaniferous groups (e.g. Cy + $\frac{1}{2}$ MeCy and Cy + Me $\frac{2}{3}$ Cy) is the same as in the simple salts, whereas the cyaniferous groups, although they contain a magnetic metal, possess a much smaller degree of magnetism, or even exhibit diamagnetism. The molecular magnetism of *potassium ferricyanide* is intermediate between those of the corresponding mangani- and cobalti-cyanides, just as in the lower oxysalts of the same metals. The magnetic powers of the three groups of cyanides just mentioned are smaller by equal amounts than those of the corresponding oxysalts. (9). The magnetic deportment of the *ferrous* and *ferric double oxalates* shows that these salts have, in the solid state as well as in solution, a constitution exactly similar to that of other ferrous and ferric salts. (10). On the other hand, the molecular magnetism of colloidal ferric oxide is only 0.22 times as great as that of ferric salts and ferric hydroxide, so that in this form of ferric oxide the magnetic group of atoms possesses properties essentially different from those which it exhibits in other forms. (11). The magnetic behaviour of *ammoniacal copper* and *nickel compounds*, as affected by alterations of density, appears to be nearly the same as that of the other oxysalts and haloïd salts of the same metals—so that the magnetic groups of atoms in these two salts must be essentially the same. On the other hand, the very feeble magnetism of the *purpureo-* and *lateo-cobaltic compounds* shows that their atomic grouping is essentially different from that of the simpler salts. (12). When considerable alterations of density take place, the magnetism of compounds in the solid state may be essentially different from that of the same compounds in solution, as in the case of cupric bromide, cobaltous chloride, &c. (13). The higher oxides of the magnetic metals (Fe²O³, &c.) are much less magnetic than the corresponding hydroxides and salts; but it is not yet determined with certainty how far this difference is due to

alterations of density or differences of atomic grouping. (14). The sulphides of the magnetic metals are for the most part much less magnetic than the corresponding salts. (15). Two diamagnetic elements (bromine and copper) may form a magnetic compound, whereas a magnetic element in combining with a nearly indifferent or slightly diamagnetic radicle (e.g. sulphur, cyanogen in the double cyanides) may lose its magnetism.

Wiedemann has also applied his observations on the magnetism of solutions to the study of the affinity of ferric oxide for acids, and the dissociation of ferric salts. It has been already stated that the molecular magnetism of colloid ferric oxide prepared by diffusion of basic ferric salts, is only about 0.22 of that of ferric oxide in strongly acidulated solutions. Further observations on solutions of recently precipitated ferric hydroxide in solutions of crystallised ferric chloride, gave for the magnetism of colloid ferric oxide a value equal to 0.2198 of that of an equal quantity of ordinary ferric oxide dissolved in ferric chloride. The observations show further that the magnetism of ferric chloride solutions containing ferric oxide is equal to the sum of the magnetisms of the iron in the chloride and in the colloid oxide; this, however, no longer holds good when basic salts are formed in the solution, the iron in these salts probably possessing an atomic magnetism peculiar to itself. If therefore in a neutral or a slightly acid solution of a ferric salt, part of the salt be resolved into free acid and dissolved colloid oxide, observations of the magnetism of the solutions will afford the means of calculating the ratio of the ferric oxide combined with the acid in the form of a salt to that of the dissolved free colloid oxide, $1-x : x$. The experiments with this object were made in the manner above described (p. 1251), excepting that the torsion-balance was made more sensitive by the use of a longer suspending wire and a stronger electromagnet. The observations made on solutions of ferric chloride of different degrees of dilution gave the following results:

Solutions of Ferric Chloride.

Iron in 10 c.c.	x	$1-x$
1.606	—	100
1.207	—	100
0.806	1.6	98.4
0.404	2.4	97.6
0.202	6.6	93.4
0.138	8.9	91.1
0.071	11.7	88.4

These numbers show that the dissociation of ferric chloride solutions increases slowly with increasing dilution. By similar observations it is found that in solutions of *neutral ferric sulphate* one-fourth of the salt is resolved into colloid dissolved ferric oxide and sulphuric acid, independently of the degree of dilution. In *ammonia-iron-alum*, one-fourth of the ferric sulphate is dissociated, independently of the ammonium sulphate. In a basic solution of *ferric nitrate*, 32 to 36 per cent. of the iron was found to be present as colloid dissolved ferric oxide. In a neutral solution of *ferric acetate* containing 0.182 gram of iron in 10 c.c., 70 per cent. of the ferric oxide was found to be dissolved in the colloid state; in neutral solution of *ferric tartrate*, 57 per cent. of the salt was dissociated (Wiedemann, *J. pr. Chem.* [2], ix. 145-171; *Phil. Mag.* [5], iv. 276).

The *hydrated peroxides of manganese, cobalt, and nickel* have but a very feeble magnetism; *chromium dioxide*, CrO_2 , on the contrary, by its very strong magnetic power, shows that it is a saline compound of chromic anhydride with chromic oxide, $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_2$. Solution of *chrome-alum* exhibits the same degree of magnetism in the violet state and in the green state produced by heat; the alteration in the colour cannot therefore be due to separation of colloid chromium sesquioxide, as this latter would be much less magnetic. In *ammonio-chromic chloride* the chromium exhibits the same magnetic behaviour as in the chromic salts: hence its constitution must be that represented by the formula $\text{Cr}_2\text{Cl}_6 \cdot 8\text{NH}_3 \cdot 2\text{H}_2\text{O}$ (*Phil. Mag.* [5], iv. 161).

Magnetism of Ilmenite (Titaniferous Iron).—This mineral may be magnetised by friction with a steel magnet, and is intermediate in its magnetic properties between iron and steel. Fine specimens from Norway of sp. gr. 4.8, containing 24.60 per cent. TiO_2 , 72.10 FeO , 2.06 FeS_2 , 1.24 SiO_2 , and a trace of manganese, were found to act on the magnetic needle, and appeared to consist of a mixture of differently oriented magnets, probably the individual crystals. A piece broken off, $1\frac{1}{2}$ inch long and $\frac{1}{4}$ inch broad, became permanently magnetised by an hour's friction with a good magnet, and when freely suspended, remained in the magnetic meridian for a month, when it suddenly lost all its polarity (T. L. Phipson, *Bull. Soc. Chim.* [2], vii. 322; *Chem. News*, xxxii. 162).

On the Magnetic Anomaly of Ferric Oxide prepared from Meteoric Iron, see IRON (p. 1097).

MAGNOCHROMITE and **GROCHAUTE**. The name magnochromite was given by von Bock in 1868 to a chrome-ore rich in magnesia, occurring in the serpentine of Grochau, near Frankenstein in Silesia. It is black, without metallic lustre, and has a brown streak. Hardness below 6. Sp. gr. = 1.4110. It forms nodules imbedded in a mountain-green matrix, which ramifies into the lumps of chrome-ore in such a manner as to render mechanical separation of the chrome-ore impossible. Perfectly pure portions of the matrix may, however, be detached from the chrome-ore. This matrix gave by analysis:

SiO ^a	Al ^a O ^a	FeO	MgO	H ^a O
28.20	24.56	5.27	30.94	12.15 = 101.12

Websky deduces from this analysis the formula $H^{10}Fe^3Mg^{51}Al^{10}Si^{11}O^{214}$. If the isomeric admixture of aluminium-hemisilicate be deducted as unimportant, the formula of the mineral will be—



It is, therefore, a new species, and Websky proposes to call it grochaute, from the locality in which it occurs. The thicker scales of the mineral contain small druses, in which the grochaute appears in six-sided tables, but its behaviour to polarised light shows that it belongs, not to the hexagonal, but to an optically biaxial system.

Deducting the composition of grochaute from that of the inseparable mixture of grochaute and magnochromite, as given by v. Bock's analysis, the remainder gives the composition of magnochromite, and shows it to be a compound belonging to the spinel group—

	SiO ^a	Al ^a O ^a	Cr ^a O ^a	FeO	MgO	H ^a O
Mixture	5.71	29.61	33.25	13.61	18.28	2.19 = 102.65
Grochaute ~ . . .	5.72	5.22	—	1.14	6.87	2.57 = 21.52
Magnochromite . .	—	24.39	33.24	12.47	11.41	— = 81.51

(Websky, *Zeitschr. geol. Ges.* xxv. 394; *Jahrb. f. Min.* 1874, 300).

MAGNOFERRITE. Intergrowths of this mineral with iron-glance, from Vesuvius, are described by G. vom Rath (*Jahrb. f. Min.* 1876, 388).

MAHONIA. The fruit of this plant yields by fermentation a very astringent wine containing 6.25 per cent. alcohol (Is. Pierre, *Compt. rend.* lxxxi. 1086).

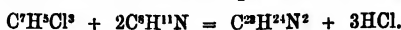
MAIROGALLOL, $C^{18}H^7Cl^{11}O^{10}$. A compound obtained, together with leucogallol, by the action of chlorine on pyrogallol dissolved in glacial acetic acid (see PYROGALLOL).

MAIZE. For the saccharification of maize and other cereals, and of lichens, &c., Colami a. Krüger make use of dilute hydrochloric acid instead of malt, the material being stirred up with water and dilute hydrochloric acid in a cylindrical copper vessel, by a current of steam under high pressure and at a temperature above the boiling point of water, but not high enough to induce the formation of caramel. The saccharification of maize requires a pressure of 3 atmospheres, under which 360 kg. of the ground grain are converted into sugar by the action of 16 kg. hydrochloric acid and 600 litres of water in 65 minutes (*Dingl. pol. J.* cxxiv. 302).

Mouldy maize-bread, treated by the Stas-Otto method (i. 125-127), yields a white non-crystalline alkaloid, which is very liable to change, and becomes coloured on exposure to the air: it is insoluble in water, but dissolves, with alkaline reaction, in alcohol and ether. Heated with sodium carbonate, it yields an alkaline distillate. Its tartrate is also easily decomposable. With sulphuric acid and oxidising agents it yields a sky-blue coloration, which disappears spontaneously after some time, but quickly and with transient violet coloration on addition of excess of water, oxidising agents, &c. With the ordinary tests for alkaloids it yields precipitates, some of which are crystalline. It resembles strychnine in its physiological action, but is not identical therewith (Lombroso, *Compt. rend.* lxxxi. 1041; *Gazz. chim. ital.* 1876, 538; Brugnatelli a. Zenoni, *ibid.* 240).

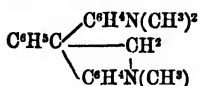
MALACHITE-GREEN (O. Doebner, *Deut. Chem. Ges. Ber.* xi. 1236). A green dye-stuff, consisting of the double zinc salt of a base having the composition $C^{23}H^{21}N^2$. It is produced on the large scale by heating 2 mols. dimethylaniline, mixed with half its weight of zinc chloride, with 1 mol. benzoyl trichloride; a deep green mass is thus produced, which may be freed from excess of the original substances by

steam. The zinc salt thus produced is soluble in water and alcohol. The free base is a red-brown uncrystallisable oil, whose salts are changed by an excess of mineral acid from green to yellow. Its formation is represented by the equation:

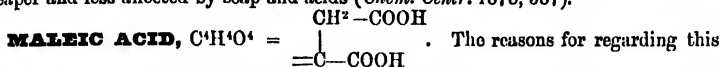


This base is reduced by zinc and hydrochloric acid, yielding a colourless base, $\text{C}^{12}\text{H}^{24}\text{N}^2$, identical with O. Fischer's tetramethyldiamidotriphenyl-methane, $\text{C}^6\text{H}^3\cdot\text{CH}[\text{C}^6\text{H}^4\text{N}(\text{CH}^3)^2]^3$, obtained by the action of benzaldehyde or benzal chloride on dimethylaniline (*Deut. Chem. Ges. Ber.* x. 1624; xi. 950): it melts, according to Doebner, at $97^\circ\text{--}98^\circ$, according to Fischer at $92^\circ\text{--}93^\circ$.

The base $\text{C}^{12}\text{H}^{24}\text{N}^2$ produced from benzotrichloride and dimethylaniline is evidently related to Fischer's base in the same manner as rosaniline to leucaniline, and may probably be represented by the constitutional formula:



Malachite-green is said to possess many advantages over methyl-green, being much cheaper and less affected by soap and acids (*Chem. Centr.* 1878, 587).



acid as an unsaturated compound, founded on its behaviour with hydrobromic acid, have already been given under FUMARIC ACID (p. 831).

Maleic acid is formed by the cautious dry distillation of silver succinate, mixed with three times its weight of sand, ($\text{C}^4\text{H}^3\text{Ag}^2\text{O}^4 = \text{Ag}^2 + \text{C}^4\text{H}^4\text{O}^4$), and passes over, partly as a highly concentrated aqueous solution which collects in the receiver, partly in crystals melting at 130° , which collect in the neck of the retort (Bourgoin, *Bull. Soc. Chim.* [2], xx. 70).

Action of Hydrobromic acid.—Maleic acid or its anhydride dissolves easily in hydrobromic acid, and the solution, even before the last particles of acid or anhydride have disappeared, deposits slender colourless needles, the quantity of which increases so rapidly that the entire liquid is soon converted into a thick crystalline pulp. The product consists of a mixture of fumaric and monobromosuccinic acids in equal numbers of molecules, whatever may have been the proportion of maleic acid and hydrobromic acid employed in the reaction. The bromosuccinic acid may be extracted from this mixture by water, which leaves it on evaporation in well-defined colourless crystals, melting at 159° , and identical in every respect with the bromosuccinic acid obtained in like manner from fumaric acid (Fittig & Dorn, *Deut. Chem. Ges. Ber.* ix. 1191).

Bromomaleic Anhydride, C^4HBrO^3 , formed by heating dibromosuccinic acid in a sealed tube to $120^\circ\text{--}150^\circ$ with acetic anhydride, melts at $125^\circ\text{--}126^\circ$, and boils at 215° (Anschütz, *ibid.* x. 1881).

Dibromomaleic acid, $\text{C}^4\text{H}^2\text{Br}^2\text{O}^4$, is formed by heating tribromosuccinic acid with water to a temperature above 100° : $\text{C}^4\text{H}^3\text{Br}^3\text{O}^4 = \text{HBr} + \text{C}^4\text{H}^2\text{Br}^2\text{O}^4$. It is a very stable compound, not being decomposed by distillation or by prolonged boiling with moist silver oxide; its silver salt also is not altered by heating with water to 120° . When, however, the acid or its silver salt is heated with water to 150° in sealed tubes, it is converted into dihydroxymaleic acid, $\text{C}^4\text{H}^2\text{Br}^2\text{O}^4 + 2\text{H}^2\text{O} = 2\text{HBr} + \text{C}^4\text{H}^4\text{O}^6$. Heated with bromine it yields carbon dioxide and tetrabromomethane: $\text{C}^4\text{H}^2\text{Br}^2\text{O}^4 + \text{Br}^2 = 2\text{CO}^2 + \text{C}^4\text{H}^2\text{Br}^4$.

Maleic Ethers.—When either maleate or fumarate of silver is left in contact at ordinary temperatures with ethyl iodide, a considerable rise of temperature takes place, and a diethylic ether, $\text{C}^4\text{H}^2(\text{C}^2\text{H}^5)^2\text{O}^2$, is formed, which boils at 218.5° (mercury-column wholly in the vapour), and is converted by saponification with alcoholic potash into fumaric acid. This result renders it doubtful whether the ether obtained from fumaric acid is really a fumarate or a maleate, and moreover throws doubt on the conclusions drawn by Hübner & Schreiber (vii. 765) from the vapour-densities of ethyl fumarate and maleic anhydride, as to the relative molecular weights of fumaric and maleic ethers (Anschütz, *Ber.* xi. 1644).

When ethyl chloromaleate (1 mol.) is mixed with a solution of potassium cyanide (3 mols.) in twice its weight of water, and sufficient alcohol to form a clear solution, the liquid becomes very hot, and potassium chloride separates out, but no cyanised compound is formed, the product when boiled with potash yielding succinic acid. Hence it appears that a reduction has taken place, a dicyanosuccinic acid being first

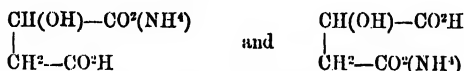
formed, which then gives off carbon dioxide and retains 2 atoms of hydrogen instead of the cyanogen-residue (A. Cluses, *Ber.* xi. 928).

Hydroxymaleic acid, $C^4H^4O^5 = COOH-CHOH-\overset{||}{C}-COOH$, is obtained by agitating a cold solution of potassium bromomaleate with recently precipitated silver oxide: $C^4HBrK^2O^4 + AgOH = AgBr + C^4H^2K^2O^5$. Separated from its lead salt by hydrogen sulphide, and crystallised from water, it forms long slender needles, and is easily soluble in water, alcohol, and ether. It is bibasic, and forms soluble salts with the alkalis and with baryta. The *silver salt*, $C^4H^2Ag^2O^5$, is insoluble in water, soluble in acids and in ammonia; it is decomposed by boiling with water, and detonates when heated. The *lead salt* is insoluble in water, even at the boiling heat, also in ammonia and the fixed alkalis, but dissolves readily in nitric acid (Bourgoin, *Bull. Soc. Chim.* [2], xix. 482).

Dihydroxymaleic acid, $C^4H^4O^6 = COOH-C(OH)_2-\overset{||}{C}-COOH$.—This acid, related to tartaric acid in the same manner as hydroxymaleic to malic acid, and maleic to succinic acid, is formed by heating dibromomaleic acid or its silver salt with water to 150° in a sealed tube for several hours: $C^4H^2Br^2O^4 + 2H^2O = 2HBr + C^4H^4O^6$. When the silver salt is used, and the liquid filtered from the precipitated silver bromide is neutralised with ammonia and mixed with silver nitrate, a white precipitate of *silver dihydroxymaleate*, $C^4H^2Ag^2O^6$, is formed, soluble in ammonia, nitric acid, and a large quantity of acetic acid, and decomposing without detonation when heated. The acid separated from this salt by hydrogen sulphide forms colourless crystals, having a strongly acid taste like that of tartaric acid, soluble in water and in alcohol, nearly insoluble in ether. The dihydroxymaleates of the alkalis and alkaline earths are soluble in water (Bourgoin, *Bull. Soc. Chim.* [2], xxii. 443).

MALIC ACID, $C^4H^4O^5 = \begin{array}{c} \text{CHOH}-\text{COOH} \\ | \\ \text{CH}^2-\text{COOH} \end{array}$. 1. *Optically Active Modi-*

fications.—The malic acid which Dessaignes obtained by the action of phosphorus iodide and water on tartaric acid (v. 675) is dextrogyrate, and has a rotatory power = $+3.157$, which is nearly equal, but opposite, to that of malic acid from mountain-ash berries (-3.299). The *acid ammonium salt* of dextromalic acid has a rotatory power = $+7.912$; that of the corresponding salt of ordinary malic acid, on the other hand, is -5.939 . If, however, the acid calcium salt of the latter acid be neutralised with ammonia, and the lime exactly precipitated by oxalic acid, an acid ammonium salt is obtained having a *laevo*-rotation = -7.816 . These facts point to the existence of two isomeric acid ammonium malates:



(G. W. Brewer, *Bull. Soc. Chim.* [2], xxv. 6; *Deut. Chem. Ges. Ber.* viii. 861; v. 1594).

Ordinary malic acid is decomposed by sulphuric acid into CO^2 , CO, H^2O , and aldehyde, $\text{C}^2\text{H}^4\text{O}$. As ethylideno-lactic acid is resolved by similar treatment into CO, H^2O , and aldehyde, it is probable that the malic acid is first converted into lactic acid, $C^4H^4O^5 = \text{CO}^2 + C^3H^4O^3$, and that the latter is then decomposed in the manner just mentioned (Weith, *Deut. Chem. Ges. Ber.* x. 1741).

Lead malate dissolves to a considerable amount in dilute acetic acid at 50° – 60° , and crystallises therefrom on slow cooling to 30° – 40° in slender needles. This reaction may be utilised for the separation of malic acid from oxalic, citric, and tartaric acid, the lead salts of which are insoluble in dilute acetic acid (F. A. Hartsen, *Arch. Pharm.* [3], vi. 110).

2. *Inactive Malic acid*.—This modification, which Pasteur obtained by the action of nitrous acid on inactive aspartic acid (iii. 789), is also produced: a. together with fumaric acid, by treating ethyl dichloropropionate with a weak alcoholic solution of potassium cyanide, and boiling the product with potash (Werigo a. Tantar, *Liebig's Annalen*, clxiv. 367). b. By heating fumaric acid with soda-ley to 100° for six hours, the reaction being apparently analogous to that which takes place in the conversion of acrylic acid into hydracrylic and ethylenelactic acids (p. 43). The *calcium salt* is precipitated by boiling from a solution prepared in the cold, in microscopic six-sided tablets, and when dried over sulphuric acid has the composition $C^4H^4CaO^5$ (Linneman a. Loidl, *Deut. Chem. Ges. Ber.* ix. 925). The *alkali-salts* of inactive malic acid are easily soluble, crystallise with difficulty, and are thrown down by alcohol as amorphous flocculent precipitates; so likewise are the *copper* and *zinc* salts. The

aqueous solution of the zinc salt becomes turbid when heated, but clear again on cooling. The *lead, silver, and mercury salts* are nearly insoluble in water, and the two latter are easily decomposed by water (Werigo a. Tantar).

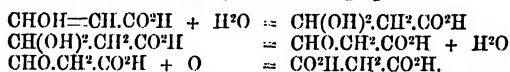
3. Isomalic or Isohydroxysuccinic Acid, $\text{CO}^2\text{H}.\text{CHOH}.\text{CH}^2.\text{CO}^2\text{H}$, is obtained by adding recently precipitated silver oxide to aqueous bromisosuccinic acid (see Succinic Acids) previously freed as completely as possible from adhering hydrobromic acid by heating in a stream of carbon dioxide, then gently heating the liquid, and separating the silver bromide by filtration. The solution freed from dissolved silver by hydrogen sulphide contains isomalic acid still contaminated with a greasy substance. For purification the acid is converted into the lead salt, which separates on adding a solution of neutral lead acetate to the aqueous or alcoholic solution of the acid, as a white, bulky, sparingly soluble precipitate. This salt, $\text{C}^4\text{H}^4\text{PbO}^5$ (dried at 120°), is distinguished from ordinary malate of lead by not melting under water. On decomposing it with hydrogen sulphide and concentrating the filtrate, isomalic acid separates in crystals, apparently monoclinic. It is easily soluble in water, alcohol, and ether, and begins to melt and give off gas at about 100° . All its salts hitherto prepared—even the acid calcium salt—are amorphous.

Isomalic acid does not react with calcium chloride and ammonia in the same manner as isosuccinic acid. When heated to 160° it is resolved into carbon dioxide and ordinary lactic acid, and has therefore the constitution of isohydroxysuccinic acid (Schmüger, *J. pr. Chem.* [2], xiv. 77).

MALIC CHLORALIDE, $\text{C}^6\text{H}^3\text{Cl}^3\text{O}^5$. See CHLORALIDE (p. 445).

MALONAMIDE, $\text{C}^3\text{H}^4\text{N}^2\text{O}^2.\text{CH}^2(\text{CONH}^2)^2$, is formed by digesting methyl malonate (p. 1259) in aqueous ammonia. On evaporating the solution, dissolving the residue in hot dilute alcohol, and leaving the liquid to cool, the malonamide separates in needles having a silky lustre. It is insoluble in absolute alcohol and in ether, and when boiled for some time in water, with repeated addition of ammonia, is converted into ammonium malonamate, $\text{CONH}^2.\text{CH}^2.\text{COO}(\text{NH}^4)$ (Osterland, *Deut. Chem. Ges. Ber.* vii. 1286). According to van't Hoff (*Arch. Néerland.* x. 274) malonamide melts at 170° .

MALONIC ACID, $\text{C}^3\text{H}^4\text{O}^4 = \text{CO}^2\text{H}.\text{CH}^2.\text{CO}^2\text{H}$. *Formation*.—1. From Ethyl Chloracrylate, $\text{C}^3\text{H}^3\text{ClO}^2.\text{C}^2\text{H}^5$. This ether is converted by prolonged boiling with baryta-water into barium acryl-lactate or hydroxyacrylate, which remains dissolved, and barium malonate which separates out; and on decomposing the mixture of barium salts thus obtained with the requisite quantity of sulphuric acid and evaporating the filtrate to a syrup on the water-bath, malonic acid crystallises out in flat prisms. Its formation from hydroxyacrylic acid, $\text{CHOH}=\text{CH}.\text{CO}^2\text{H}$, produced in the first instance, may perhaps be represented by the following equations:



The oxygen may be supposed to be derived from the air. Malonic acid is also said to be contained, together with a second acid, in the water which passes over on distilling crude ethyl chloracrylate in a current of steam.

2. Malonic acid is formed in small quantity, together with much carbon dioxide and oxalic acid, by the oxidation of ethylene-lactic acid with chromic acid (Wislicenus, *Liebig's Annalen*, clxvii. 346).

3. From Mucobromic acid, $\text{C}^4\text{H}^2\text{Br}^2\text{O}^3$. The acid which Schmelz a. Beilstein obtained by the action of bromine and water on pyromucic acid (iii. 763) was supposed by them to be resolved by boiling with excess of baryta-water into carbon dioxide, hydrogen bromide, bromacetylene, and an acid, $\text{C}^3\text{H}^2\text{O}^3$, which they designated as *muconic acid*. Jackson a. Hill, however, find that the lead salt of the acid thus obtained has the composition $\text{C}^3\text{H}^2\text{PbO}^4$, and that the acid separated from it is identical in every respect with malonic acid prepared from cyanacetic acid. They find also that mucobromic acid treated with baryta-water yields bromide and formate of barium, as well as malonate, so that the reaction may be represented by the equation:



Preparation.—The ethyl cyanacetate required for the preparation of malonic acid (iii. 799) is best obtained, according to Franchimont (*Deut. Chem. Ges. Ber.* vii. 216), from ethyl bromacetate. This latter, obtained by boiling bromacetic acid for an hour in the water-bath with absolute alcohol, is washed several times with water, dissolved in about ten times its volume of alcohol, and pure pulverised potassium cyanide is then added to it in excess. The liquid soon boils, and the odour of the ethyl brom-

acetate disappears after a short time. It is then filtered to separate potassium bromide, caustic potash is added, the alcohol is distilled off, and the aqueous solution boiled as long as it continues to give off ammonia. The malonic acid is best extracted from the residue by acidulation and agitation with ether. A small quantity of succinic acid is formed at the same time.

Conrad (*Ber.* xi. 749) dissolves monochloroacetic acid in a small quantity of alcohol and neutralises it with dilute soda-ley, keeping the liquid cool; then adds an equivalent quantity of potassium cyanide dissolved in water, whereupon cyanacetate of alkali-metal is formed with great rise of temperature; and heats the liquid for several hours to complete the reaction. On subsequent addition of a quantity of soda-ley equal to that which was used for the neutralisation of the chloroacetic acid, a copious evolution of ammonia takes place after some minutes, attended with sudden ebullition. After all the ammonia has been driven off by prolonged boiling, the solution may be neutralised with hydrochloric acid, and the malonic acid precipitated by calcium chloride.

On the preparation of malonic acid, see also Petrieff (*Ber.* vii. 400); van 't Hoff (*ibid.* 1571); Osterland (*ibid.* 1286); H. v. Miller (*J. pr. Chem.* [2], xix. 326).

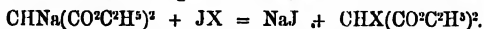
Electrolysis.—A solution of 100 grams malonic acid in 200 c.c. water, neutralised with potassium carbonate and subjected to the action of a battery of six Bunsen's cells, yields nothing but carbon dioxide and hydrogen, the methylene liberated in the first instance (succinic acid similarly treated yields ethylene) being probably oxidised by nascent oxygen (v. Miller).

Malonic Ethers. When *ethyl malonate*, $\text{CO}^2\text{C}^2\text{H}^3.\text{CH}^2.\text{CO}^2\text{C}^2\text{H}^3$, is treated with 1 mol. potassium hydroxide, both dissolved in alcoholic potash, the whole solidifies to a crystalline pulp of potassium ethylmalonate, which is decomposed by phosphorus pentachloride, yielding ethyl chloromalonate, according to the equation:

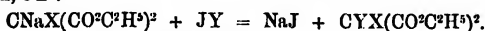


Ethyl chloromalonate boils between 170° and 180° , and is decomposed by water, like an acid chloride, the resulting liquid, when heated with potash, yielding ethyl alcohol (J. van 't Hoff, *Deut. Chem. Ges. Ber.* vii. 1571).

Ethyl malonate, like ethyl acetate, is capable of taking up 1 or 2 atoms of sodium. The reaction begins, with evolution of hydrogen, at ordinary temperatures, but is much retarded by the crust of sodium-compound which forms on the surface of the metal. This, however, may be prevented by adding absolute alcohol (2 vol. to 1 vol. of the ethyl malonate) which holds the sodium in solution. As the liquid cools, the sodium-compound of the malonic ether separates as a crystalline mass. If required to be free from alcohol, it must be heated to 150° on an oil-bath in a flask through which a brisk current of dry hydrogen is passed; if, however, it is wanted merely for synthetical purposes the presence of alcohol is for the most part not injurious, and the sodium compound may be subjected to the action of an organic halogen-compound as soon as the sodium is dissolved. The action is usually very energetic, but prolonged heating on the water-bath is necessary for its completion, which may be recognised by the fact that a drop of the mixture no longer blues moistened red litmus paper. Water is then added to dissolve the haloid sodium-compound, and the oil which then separates is submitted to fractional distillation. The yield of the organic substituted malonic ether thus obtained is very nearly equal to that required by the following equation, in which X denotes an organic residue, and J the substituted halogen:

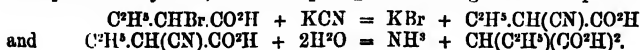


From this primary substitution-product, a secondary substitution-product may be obtained as in the case of the aceto-acetic ethers (p. 13), by replacing the remaining hydrogen-atom in the group CHX by sodium, and treating the product with another organic halogen, JY:



Ethylid Ethylmalonate, $\text{CH}(\text{C}^2\text{H}^3)(\text{CO}^2\text{C}^2\text{H}^3)^2$, thus prepared (with 15 grams of absolute alcohol, 2.3 sodium, and 16 $\text{C}^2\text{H}^3\text{J}$) distilled over between 208° and 210° . On saponifying this ether with potash, acidulating, and agitating with ether, ethylmalonic acid, $\text{C}^3\text{H}^4\text{O}^4$, separates in the form of a crystalline mass (Conrad, *Deut. Chem. Ges. Ber.* xi. 750).

ETHYLMALONIC ACID, $\text{C}^3\text{H}^4\text{O}^4 = \text{CH}(\text{C}^2\text{H}^3)(\text{CO}^2\text{H})^2$, metameric with pyrotartaric acid, and likewise called *α -isopyrotartaric acid*, was first obtained by Wislicenus in 1869 (*Liebig's Annalen*, cxlix. 220), who prepared it by treating ethyl bromobutyrate with potassium cyanide, and decomposing the resulting nitril with potash:



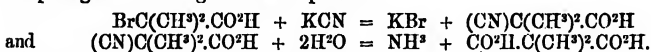
The acid thus obtained was a syrupy liquid. Subsequent experiments by Wislicenus a. Urech (*ibid.* clxv. 93) showed, however, that this syrup was a mixture of ethylmalonic acid with a small quantity of oxybutyric acid, and that the former may be separated in the crystalline state by leaving the syrupy acid at rest for some time, or better by converting it into a copper salt, purifying this salt by repeated crystallisation, and decomposing it with hydrogen sulphide.

Ethylmalonic acid is also produced from ethyl cyanobutyrate by the action of hydrochloric acid, or better of potash, since it is decomposed by hydrochloric acid in the subsequent evaporation. Its aqueous solution likewise decomposes when evaporated at too high a temperature, giving off carbon dioxide and butyric acid vapour. By slow crystallisation it is obtained in rhombic prisms, sometimes a centimeter long. From warm solutions, or by rapid crystallisation, it separates in feathery groups resembling sal-ammoniac. It dissolves easily in water, alcohol, and ether, melts at 111.5° , and decomposes without sublimation at 160° (or more quickly at 170°) into carbon dioxide and butyric acid.

Potassium ethylmalonate separates on mixing the alcoholic solutions of the acid and potassium hydroxide in small crystals, easily soluble in water, insoluble in alcohol. The sodium salt separates from concentrated solutions in granular masses, effloresces in contact with the air, and dissolves easily in water, more freely however in cold than in hot water (Markownikoff, *Liebig's Annalen*, clxxxii. 324). The barium salt is anhydrous, and crystallises in small needles. The calcium salt, $C^5H^4O^4Ca + H^2O$, crystallises in prisms, and is more soluble in cold than in hot water (Tupoleff, *Deut. Chem. Ges. Ber.* vi. 1440).

The zinc salt, $C^5H^4O^4Zn + 2\frac{1}{2}H^2O$, is especially characteristic; it dissolves but sparingly in water, whether hot or cold, and separates on evaporation as a crystalline powder made up of hexagonal or quadratic (rhombic?) plates. At the moment of its formation it dissolves more readily, and then separates on cooling (also by slow evaporation of cold solutions) as a crystalline crust (Markownikoff, *loc. cit.* According to Wislicenus a. Urech (*ibid.* clxv. 93) this salt, prepared by saturation or by precipitation, contains 3 mols. H^2O , and gives off only $2\frac{1}{2}$ mols. at 150° . The copper salt, $C^5H^4O^4Cu + 3H^2O$, forms blue-green tablets, which give off only $2\frac{1}{2}$ mols. H^2O at 150° . The lead salt, $C^5H^4O^4Pb$, is formed on precipitating a solution of the ammonium salt with lead acetate (W. and U.) The ethylic ether, $C^5H^4O^4(C^2H^5)^2$, already mentioned (p. 1258) may also be prepared by decomposing the silver salt with ethyl iodide, and forms a colourless liquid having a faint aromatic odour and boiling, after repeated rectification, at 199° – 201° (uncorr.) At a higher temperature (250° – 300°) it is partially decomposed with formation of ethyl butyrate (Markownikoff).

DIMETHYL-MALONIC ACID, $C^5H^8O^4 = CO^2H.C(CH^3)^2.CO^2H$. β -Isopyrotartaric acid (Markownikoff, *Deut. Chem. Ges. Ber.* vi. 1440; *Liebig's Annalen*, clxxxii. 324). This acid is formed by heating bromisobutyric acid with potassium cyanide, and decomposing the resulting nitril with potash:



It crystallises in transparent four-sided prisms, sparingly soluble in alcohol, moderately soluble in water, though less so than its isomerides, pyrotartaric and α -isopyrotartaric or ethyl-malonic acid. At about 120° it sublimes in white needles resembling sal-ammoniac, and at about 170° it begins to melt, and split up into isobutyric acid and carbon dioxide. It is not attacked by boiling dilute nitric acid, and scarcely at all by boiling chromic acid mixture. The mother-liquors obtained in its preparation appear to contain oxyisobutyric acid.

Sodium dimethylmalonate forms small efflorescent needles, slightly soluble in water. The barium salt is less easily soluble, and crystallises in stellate groups of thin needles. The calcium salt, like that of the α -acid, is moderately soluble in cold water, and is deposited from the solution on warming. It crystallises in nodules. The magnesium salt is crystalline, and easily soluble in water. The zinc salt, $C^5H^8O^4Zn.3H^2O$, obtained by saturating the acid with zinc carbonate, dissolves in 106 parts of water. It resembles the zinc salt of the α -acid, and decomposes in the same manner. The lead salt, produced on adding lead acetate to a hot solution of the sodium salt, forms white scales, insoluble in hot and cold water. The silver salt crystallises in small needles, insoluble in water and not affected by boiling.

METHYL MALONATE, $C^5H^8(CH^3)O^4$, obtained by the action of methyl iodide on silver malonate, is a mobile liquid having an ethereal odour, a specific gravity of 1.135 at 22° , boiling at 175° – 180° , and remaining fluid at -14° . Its vapour-density ($H = 1$) is 66.79 (calc. 66). It is insoluble in water, by which, however, it is gradually decomposed; soluble in alcohol and ether. Ammonia converts it into malonamide (Osterland, *Deut. Chem. Ges. Ber.* vii. 1286).

Bromomalonic acids. The *monobrominated acid*, $\text{CHBr}(\text{COOH})^2$, obtained by the action of sodium-amalgam on an aqueous solution of the dibrominated acid, crystallises in large square plates, which dissolve easily in alcohol, forming acid ethyl bromomalonate, $\text{CO}^2\text{H}.\text{CHBr}.\text{CO}^2\text{C}^2\text{H}^3$, which may also be formed directly by the action of sodium-amalgam on an alcoholic solution of dibromomalonic acid (W. Petrieff, *Deut. Chem. Ges. Ber.* xi. 414).

Dibromomalonic acid, $\text{CBr}^2(\text{CO}^2\text{H})^2$, is formed in small quantity by the action of bromine, aided by heat, on an aqueous solution of malonic acid. The action is attended with evolution of hydrobromic acid, together with a large quantity of a colourless gas, and the principal product is a heavy neutral oil (Petrieff, *Ber.* vii. 400). According to van 't Hoff (*ibid.* viii. 355), the colourless gas is carbon dioxide, and the oily liquid consists of bromoform, which, however, is not a constant product of the reaction. A concentrated solution of malonic acid is attacked by bromine, even at ordinary temperatures, with considerable evolution of heat. At the end of the reaction, tribromacetic acid separates as a white crystalline mass, and the mother-liquor contains dibromacetic acid together with a very small quantity of dibromomalonic acid.

Hydroxymalonic or Tartronic acid, $\text{C}^3\text{H}^4\text{O}^5 = \text{CH}(\text{OH})(\text{CO}^2\text{H})^2$. This acid was discovered by Dessaignes, who obtained it by the spontaneous decomposition of nitrotartaric acid, and by the action of sodium on mesoxalic acid (v. 698). Demole (*Deut. Chem. Ges. Ber.* x. 1788) prepares it by gradually adding 20 grams of nitrotartaric acid to 60 c.c. alcohol of sp. gr. 0.925 in a porcelain basin on the water-bath, and leaving the liquid to cool after the evolution of gas has ceased. The crystals which separate are pressed between filter-paper and dissolved in water, the solution evaporated to dryness, and the residue treated with ether to separate oxalic acid. The acid thus obtained melts at $150^\circ\text{--}151^\circ$; Grimaux (*Ber.* x. 903), who prepared it by treating dibromopyruvic acid with baryta-water, found that it melted at $145^\circ\text{--}147^\circ$.

Tartronic acid is also produced by the action of silver oxide on monobromomalonic acid, and by heating the product of the action of potassium cyanide on dibromacetic acid with potassium hydroxide (Petrieff, *Ber.* x. 414).

Dihydroxymalonic acid, $\text{C}^3\text{H}^4\text{O}^6 = \text{C}(\text{OH})^2(\text{CO}^2\text{H})^2$. The *barium salt* of this acid, $\text{C}(\text{OH})^2(\text{CO}^2)^2\text{Ba}$, is formed by boiling the solution of the dibromomalonate, and keeping it neutral by repeated addition of baryta-water. It then separates as a white crystalline salt, and crystallises from solution in a small quantity of hot water, in short white needles easily soluble in acids. The *calcium salt* is a white amorphous precipitate. The *silver salt* is a flocculent precipitate which dissolves in nitric acid and in ammonia, and decomposes with explosion when heated. The acid prepared from the barium salt by evaporation with hydrochloric acid and extraction with ether, crystallises, though at first with some difficulty, from its aqueous solution acidulated with hydrochloric acid. By recrystallisation from ether it is obtained in radiate groups of needles which melt at 96° , and dissolve readily in water, alcohol, and ether.

Mesoxalic acid, which is produced by oxidation of amidomalonic acid (iv. 115), has hitherto been regarded as $\text{C}^3\text{H}^2\text{O}^5$, its salts in the anhydrous state being represented by the formula $\text{C}^3\text{M}^2\text{O}^5$. According to Deichsel's analyses, however (vi. 825), all these salts, except the ammonium salt, contain at least 1 mol. H^2O , and might therefore be equally well represented by the formula $\text{C}^3\text{H}^2\text{M}^2\text{O}^6$, according to which the acid would be $\text{C}^3\text{H}^4\text{O}^6$, that is to say dihydroxymalonic acid. The ammonium salt, however, appeared to contain 1 mol. H^2O less than the other mesoxalates, a fact which if established would be inconsistent with this view of the composition of the acid; but Petrieff, by saturating an aqueous solution of mesoxalic acid with ammonium carbonate, and evaporating the solution in a vacuum, has obtained ammonium mesoxalate in colourless needles analogous in composition to the other mesoxalates, that is to say, represented by the formula $\text{C}^3(\text{NH}^1)^2\text{O}^5.\text{H}^2\text{O}$ or $\text{C}^3.\text{H}^2(\text{NH}^1)^2\text{O}^6$. Deichsel's salt, which formed granular crystals turning red in the air, was probably the corresponding monamide, $\text{C}^3\text{N}^2\text{H}^3\text{O}^5 = \text{C}^3\text{H}^2(\text{NH}^1)^2\text{O}^6 - \text{H}^2\text{O}$; and this view is in accordance with the manner in which it was prepared, namely, by the action of ammonia on an alcoholic solution of mesoxalic acid, as such a solution would probably contain ethyl mesoxalate, which with ammonia would yield the amide. The property which Deichsel's compound exhibits, both in the solid state and in solution, of turning red in the air, affords another argument in favour of this view of its constitution, the same property being exhibited by the diamide which Petrieff obtained by the action of ammonia on ethyl mesoxalate.

That mesoxalic acid really contains two hydroxyl-groups attached to the same carbon-atom is shown by the formation of diethylic diacetomesoxalate, $\text{C}(\text{OC}^2\text{H}^3\text{O})^2(\text{COOC}^2\text{H}^3)^2$. This ether, prepared by heating 2 mols. acetyl chloride

with 1 mol. ethylmesoxalate for an hour in the water-bath, crystallises in long white needle-shaped crystals, melting, with partial decomposition, at 145° , partly decomposed by solution in water, completely by agitation with a weak alcoholic alkaline ley. The diacetomesoxalic acid thereby produced crystallises in needles, melts at -130° , and decomposes at a higher temperature. Its alkali-salts are crystallisable and easily soluble in water; the silver and lead-salts are insoluble pulverulent precipitates. Finally, mesoxalic acid agrees in all its properties with the dihydroxymalonic acid which Petrieff obtained by the action of baryta-water on barium dibromomalonnate (Petrieff, *loc. cit.*)*

MALT. On the preparation of Malt extract, see Jassey (*N. Jahrb. Pharm.* xxxix. 150; *Jahresb. f. Chem.* 1873, 1076).

On the Malt-test and Mash-process, see Lintner (*Dingl. pol. J.* ccxviii. 182; *Jahresb. f. Chem.* 1875, 1131); also W. Schultze (*Dingl. pol. J.* ccxxxi. 53; *Chem. Soc. J.* xxxiv. 569).

MALTOSE. See SUGARS.

MALYLURAMIDE and **MALYLUREIDIC ACID.** See URIMIDOSUCCINAMIDE and URIMIDOSUCCINIC ACID, under SUCCINIC ACID.

MANDELIC ACID, $C^8H^8O^3 = C^6H^5.CH(OH).CO^2H$. This acid is formed by reduction of phenylglyoxylic acid, $C^6H^5.CO.CO^2H$, with sodium amalgam (Schwobel, *Deut. Chem. Ges. Ber.* x. 2045). On its preparation from benzoic aldehyde, acid sodium sulphite, and potassium cyanide, see O. Müller (*vii.* 767). It melts at 115° (Müller, *Arch. Pharm.* [3], ii. 385).

On *Mandelic Chloralide*, see CHLORALIDE (p. 445).

MANGANESE. Ores. The lithia psilomelane of Salm-Chateau in Belgium has been analysed by H. Laspeyres (*J. pr. Chem.* [2], xiii. 1) with the following results:

1. Mean of two analyses. 2. Reduced to 100, the excess being distributed nearly in proportion to the values of the several constituents:

	SiO ²	CnO	CoO	CaO	MgO	Al ² O ³	Fe ² O ³	MnO
(1.)	0.132	0.080	0.119	0.262	0.078	2.525	0.173	75.741
(2.)	0.129	0.078	0.116	0.255	0.026	2.458	0.168	73.728
	K ² O	Na ² O	Li ² O	O	H ² O	Sp. gr.		
(1.)	3.379	0.835	0.481	14.658	3.764 = 102.227		4.328 at 18.2°	
(2.)	3.289	0.813	0.468	14.658	3.764 = 100		4.277 at 16.8°	

From this analysis, Laspeyres infers that psilomelane is a manganate of the bases $3R''O$, $3R'O$ and R^4O^2 , in which $R'' = Mn, Cu, Co, Ca, Sr, Mg$; $R' = H, K, Na, Li$; $R^4 = Al$ and Fe , the corresponding manganic acid being H^4MnO^3 or $2H^2O.MnO^3$. The older analyses of psilomelane (*iii.* 813) exhibit considerable divergence from this formula, but the differences range themselves about equally on both sides of it, so that it may be regarded as representing the average composition of the mineral.

Laspeyres (*ibid.* 176) has further extended this mode of representation to all varieties of manganese peroxide, natural and artificial, and classifies them as in the following table, the manganese of the base (bivalent) being denoted by mn, and that of the acid (sexvalent) by Mn:

Pyrolusite and Polianite, $mn.MnO^4$	type H^2MnO^4
Psilomelane, H^4mnMnO^5	„ H^4MnO^5
Groröilite, H^4mnMnO^6	}	„ H^6MnO^6
Varvite, $H^2mn^2MnO^6$		„ H^6MnO^6
Braunite (Marcelin), mn^2MnO^6		„ H^6MnO^6
Cupreous Manganese, $H^4R''mnMnO^7$, where $R'' = mn, Cu, \&c.$	„ H^6MnO^7
Manganite, $H^4mn^2MnO^8$	}	„ $H^{10}MnO^8$
Wad, $H^4mn^2MnO^8$		„ $H^{10}MnO^8$
Hausmannite, mn^2MnO^8		„ $H^{10}MnO^8$
Earthy Cobalt, $H^4R''mnMnO^9$	}	„ $H^{12}MnO^9$
„ $R'' = Co, Cu, \&c.$		„ $H^{12}MnO^9$
Crednerite, $Cu^4mn^2MnO^9$		„ $\alpha(H^2O)$
Pyrochroite, H^4mnO^7	„ $\alpha(H^2O)$

Laspeyres (*ibid.* 215) has also discussed the constitution of aluminiferous manganese ores, basing his calculations on an exact analysis of psilomelane with hæmatitic struc-

* The discussion respecting the composition of mesoxalic acid is exactly analogous to that which has taken place respecting glyoxylic acid, $C^2H^2O^3$ or $C^2H^2O^4$ (p. 891).

ture from Kaltebsen near Eisenfeld. This mineral occurs on lepidocrocite, limonite, or quartz, especially on the former, with which it is very intimately interstratified:

SiO ²	CuO	CoO	CaO	BaO	MgO	Al ² O ³	Fe ² O ³	MnO
0.365	1.150	0.467	0.096	0.198	0.197	6.322	3.769	67.870
K ² O	Na ² O	Li ² O	O	H ² O	Sp. gr.			
0.384	0.389	0.210	13.662	6.420	= 101.499			4.361 at 14°.

Also traces of strontium, but no nickel or vanadium.

The ferric oxide may be deducted as lepidocrocite, also the silica. The alumina, on the other hand, must be regarded as an essential constituent of the mineral, inasmuch as the quantity of silica present is not sufficient to justify the supposition of its existence in the form of admixed silicate, and, on the other hand, its solubility in dilute hydrochloric acid is inconsistent with its presence as corundum, diaspor, &c. Admitting that there is an excess in the estimation of the bases (from admixed silicate) and of the water (partly hygroscopic, as the mineral left in the exsiccator for sixteen days lost 0.358 per cent.), the analyses lead to the supposition that the mineral is a manganate derived from the acid $\text{H}^{10}\text{Mn}^6\text{O}^{11}$, and intermediate between those of the type H^4MnO^3 (psilomelane) and those of the type H^6MnO^6 (braunite, &c.) Laspeyres proposes to designate it as *Calvonigrite*.

Among former analyses of aluminiferous manganese ores, only that by Winkler (vii. 756) of a *lithiophorite* from Schneeberg appears to belong to a definite manganate of the type $\text{H}^{10}\text{MnO}^{11}$.

A *cupreous manganese* from Chile, occurring intergrown with chrysocolla, and possibly identical with Richter's pelconite (iii. 814), has been analysed by Frenzel (*Jahrb. f. Min.* 1873, 801). Sp. gr. 2.95 at 20°. a. Analysis. b. Composition after deduction of the residue.

	O	CuO	CoO	MnO	Fe ² O ³	BaO	CaO	MgO	H ² O	Residue
a. 5.16	18.68	4.70	26.31	8.10	0.55	0.75	2.33	19.40	15.60	= 101.58
b. 6.10	22.07	5.55	31.08	9.57	0.65	0.89	2.74	22.92	—	= 101.58

A considerable number of manganese ores from the Arschitzaberg in the Bukowina, which have lately acquired great industrial importance, have been analysed by Morawski a. Stingl (*J. pr. Chem.* [2], xv. 228):

1. Soft, friable, fissured, strongly staining bluish-black masses. 2. Botryoidal, compact sealy masses having a strong lustre. 3. Stalactitic crust on a massive ore. 4. Micro-botryoidal, with irregularly conchoidal, highly lustrous fracture. 5. Principal mass of the commercial ore, compact, massive, bluish-black. 6. Porous mass, made up of quartz-veins and a yellow earthy substance consisting of iron phosphate and manganese dioxide. 7. Shaly masses, the layers of which alternate with the variety described under No. 4. 8. Transformation-product of No. 9. 9. Crystalline rose-red siliceous manganese often coated with an amorphous black-brown product of transformation (No. 8). 10-12. Silicates from Nos. 4, 5, and 7, obtained by decomposing considerable quantities of these ores with hydrochloric acid:

	1	2	3	4	5	6	7	8
O	15.75	15.04	14.75	13.88	13.39	7.66	1.50	38.87 (1)
MnO	75.07	71.81	73.98	68.74	66.41	36.71	7.15	5.30
Fe ² O ³	4.97	6.81	2.36	2.67	10.23	11.45	6.22	5.25
CaO	1.05	0.77	1.26	0.47	0.74	0.72	0.73	0.61
MgO	trace	trace	0.13	0.13	0.16	trace	0.23	0.30
Na ² O	0.58	1.37	1.79	1.23	1.32	0.59	1.53	0.21 (2)
H ² O	2.87	2.93	4.22	3.00	4.69	4.34	2.16	7.15
P ² O ⁵	0.96	0.91	0.95	0.34	0.87	0.29	0.38	—
SiO ² (soluble)	0.55	0.56	0.45	0.68	0.41	0.74	79.99	29.42
Silicate	—	1.26	0.29	8.88	1.63	38.44		13.56
Total	101.80	100.96	100.18	100.02	99.85	100.94	99.89	100.67
MnO ²	85.65	81.80	80.20	75.52	72.81	41.66	8.18	38.87
MnO	5.17	5.05	8.53	7.10	6.99	2.71	0.47	5.30
H ² O at 100°. 110°	1.82	1.00	2.22	0.68	3.43	2.01	0.65	undet.
Sp gr	4.435	4.471	3.882	3.979	4.027	undet.	2.661	undet.

(1) MnO².

(2) Alkalies.

	SiO ^a	MnO	FeO	CaO	MgO	Na ^a O	P ^a O ^a		Sp. gr.
9.	48.11	43.17	4.31	3.00	1.73	0.13 (1)	trace	= 100.45	3.624
10.	85.40	5.82	6.67	1.87	0.75	0.30	—	= 100.51	—
11.	85.93	7.80	3.16	1.83	0.29	0.81	—	= 99.82	—
12.	99.15	0.11	1.02	trace	trace	—	—	= 100.28	—

(1) Alkalis.

In the following calculation of the numbers 1 to 5, the silicate, soluble silicic acid, and phosphoric acid are deducted, whilst the dioxide and monoxide of manganese, together with the ferric oxide, lime, magnesia, alkalis, and water are regarded as essential constituents of the ores. Calculating in this way and reducing all the metal-atoms to bivalence, the following proportions are obtained:

	(1)	(2)	(3)	(4)	(5)	
R''	1	1	1	1	1	
O.	1.79	1.71	1.68	1.71	1.60	
or:						Mean
R''	3	3	3	3	3	3
O.	5.37	5.15	5.05	5.15	4.80	5.10

The first series of numbers shows that these ores must be regarded as psilomelanes, a conclusion which agrees with their other constituents and with their properties; and the second series shows that they may be included in the formula 11^aMnO^3 laid down by Laspeyres (p. 1261), if this formula be generalised in the form $R^3\text{O}^3$, by writing $R'' = 11^a$. The silicates mixed with the samples 4 and 5 consist, as shown by analyses 10 and 11 compared with 9, of altered rhodonite (v. 106), which, as manganous carbonate is not found in the neighbourhood of these ores, may be regarded as the original mineral from which the psilomelanes have been formed. The residue No. 12 from No. 7, consists essentially of quartz.

Reactions. 1. *Precipitation as Dioxide.*—From a solution of manganous chloride mixed with a certain amount of ferric chloride, the whole of the manganese may be precipitated as dioxide by a sufficient excess of solution of *calcium hypochlorite* or *bromine-water*, the solution being heated to $140^\circ\text{--}150^\circ\text{F.}$ ($60^\circ\text{--}71^\circ\text{C.}$), an excess of calcium carbonate added, and the mixture well stirred. Without the ferric salt, the precipitation of the manganese as dioxide is incomplete. Zinc chloride may be substituted for ferric chloride, but neither aluminium chloride nor barium chloride has the same effect (J. Pattinson, *Chem. Soc. J.* xxxv. 365).

Manganese may also be precipitated as dioxide from acetic acid solution by *hydrogen dioxide*. In applying this method to analytical purposes, the solution should be warm and carefully neutralised, if necessary, with ammonia. Iron if present must be previously removed by precipitation with sodium acetate (Rosenthal, *Dingl. pol. J.* cxxv. 154).

2. Manganous oxide, either precipitated or crystalline, and precipitated manganese dioxide, are converted by yellow *ammonium sulphide* into sulphides (Priwoznik, *Deut. Chem. Ges. Ber.* 1873, 1291).

3. By fusing any manganese compound (free from iron) with silica and baryta or a mixture of soda and lime, a blue compound is obtained, the intensity of the colour of which depends on the quantity of manganese used, but it may be changed to green or violet by adding different quantities of alkali or silica. The blue compound, which appears to be a silico-manganate of the alkaline earths, is destroyed by reducing agents, by acids, and after some time by water, but resists a temperature of 1100° . This reaction is proposed as a means of detecting traces of manganese in minerals (G. Bong, *Bull. Soc. Chim.* [2], xxix. 199).

4. *Detection in Plant-ashes.*—According to G. Campani (*Gazz. chim. ital.* 1876, 464) manganese occurs in plant-ashes chiefly in the form of phosphate. On treating the ashes with water and then with nitric acid free from phosphoric acid, there remains after evaporation of the latter solution, a residue which is amethyst or violet coloured according to the quantity of this metal present. This reaction will serve to detect 1 pt. of manganese in 1000 pts. of ash.

Estimation. 1. *By Electrolysis.*—The manganese solution is placed in a platinum crucible, which serves as positive electrode, the negative being formed of a spiral of platinum wire. The manganese is deposited on the crucible in the form of dioxide. The accuracy of the result is not impaired by the presence of copper, cobalt, nickel, zinc, magnesium, aluminium, or of alkalis or alkaline earths, but iron-salts must be previously removed. By this method 0.0005 grm. of Mn^aO^1 can be easily estimated and 0.000025 grm. detected by the rose coloration which it exhibits (A. Riche, *Compt. rend.* lxxxv. 226; *Chem. Soc. J.* xxxiv. 750).

2. *By precipitation as Oxalate.*—The solution is mixed with a strong solution of potassium oxalate (1 : 6), and then with strong alcohol or acetic acid, whereupon the whole of the manganese is precipitated as manganous oxalate, mixed, however, with potassium oxalate, which must be removed by washing. The best mode of proceeding is to add to the concentrated solution of the manganese salt, first potassium oxalate and then strong acetic acid, as long as a precipitate continues to form. The presence of hydrochloric acid, ammonium chloride, or potassium chloride, in considerable quantity, renders the results inexact (Classen, *Zeitschr. anal. Chem.* 1877, 315, 470).

If the solution, after addition of the potassium oxalate, be rendered ammoniacal and then mixed with ammonium sulphide, the precipitated manganous oxalate will be converted into anhydrous manganous sulphide. The presence of ammonium chloride does not interfere with the reaction (Classen, *ibid.* 319).

3. The following volumetric method, founded on the precipitation of manganese as dioxide in presence of ferric chloride (p. 1263), is recommended by J. Pattinson (*Chem. Soc. J.* xxxv. 368). The reagents employed are: (1). The clear liquid obtained by decantation from a 1·5 per cent. solution of bleaching powder; (2) light granular calcium carbonate obtained by precipitating an excess of calcium chloride with sodium carbonate at 180° F.; (3) a 1 per cent. solution of ferrous sulphate in dilute (1 in 4) sulphuric acid; (4) a standard solution of potassium dichromate equivalent to 1 part of iron in 100 of solution. The application of the process to manganiferous iron ores is as follows: 10 grains of the ore, dried at 212° F., are dissolved in a 20-oz. beaker in about 100 fluid grains of hydrochloric acid (sp. gr. 1·18). Calcium carbonate is then added until the free acid is neutralised and the liquid turns slightly reddish. 6 or 7 drops of hydrochloric acid are now added, and 1000 grains of the bleaching-powder solution, or 500 grains of saturated bromine-water, and boiling water is run in until the temperature is raised to 140° to 160° F.; 25 grains of calcium carbonate are added, and the whole is well stirred. If the supernatant solution has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated oxides of iron and manganese are filtered off and washed; 1000 grains of the acidified ferrous sulphate solution are carefully measured into the 20-oz. beaker already used; and the filter with its washed contents is added. A certain quantity of the ferrous sulphate is oxidised by the MnO^2 ; this quantity is estimated with the standard dichromate solution, and the quantity of MnO^2 can then easily be calculated. The iron present must be at least equal in weight to the manganese during the precipitation, in order to ensure the absence of lower oxides. The method is applicable to the analysis of spiegeleisen, ferro-manganese steel, and manganese slags.

For other volumetric methods, see Morrell (*Amer. Chem.* vi. 45); Morawski a. Stigl (*J. pr. Chem.* [2], xviii. 96; *Chem. Soc. J.* xxxvi. 277); Kessler (*Zeitschr. anal. Chem.* 1879, 1; *Chem. Soc. J.* xxxvi. 342); and for the estimation of manganese in Iron and Steel, see pp. 1103 and 1104 of this volume.

Alloys. Terrell (*Bull. Soc. Chim.* [2], xxi. 289) has obtained alloys of manganese by the action of certain metals on anhydrous manganous chloride (prepared by igniting the well-dried hydrated chloride in a stream of hydrochloric acid gas). The *aluminium alloy* Mn^3Al scratches glass, and has a fracture like that of amalgamated zinc. The *magnesium alloy* is less hard. The action of zinc on manganous chloride is attended with explosion.

Manganese-bronze.—An alloy thus named, and said to be a compound or mixture of ordinary bronze with manganese, is manufactured by the White Brass Company in Southwark. Its fracture resembles that of fine-grained steel; it is capable of acquiring considerable hardness, and in colour and lustre it resembles good gun-metal. At a red heat, it can be forged, rolled, and drawn into wire and tubes. Experiments on the tenacity of several bars of this metal gave for the cast material an absolute tenacity and extensibility equal to that of bar-iron of medium quality, while its limit of elasticity was higher. Forged samples excelled the best bar-iron in tenacity and extensibility, and were in these respects equal to soft steel (*Dingl. pol. J.* cccxi. 334).

Alloys of Manganese and Iron.—Numerous analyses of spiegeleisen (with less than 26 per cent. Mn) and ferromanganese (with more than 26 per cent. Mn) are given under IRON (pp. 1109–1111).

Rosenthal (*Dingl. pol. J.* cccxiv. 654) has analysed two specimens of English manganiferous iron prepared by a new process, with the following results:

	Fe	Mn	Si	C	S	P
I.	58·54	30·14	9·775	1·739	—	0·051
II.	60·10	28·89	8·812	2·131	0·009	0·048

On fusing the first of these alloys in the cupola-furnace, nearly all the silicon and half the manganese were eliminated, and the proportion of carbon was increased by 5 per

cent. The mass, which was at first white and brittle, then exhibited the ordinary properties of spiegeleisen.

According to P. Ward (*ibid.* cccxvi. 53), the blast-furnace of Reohitza, in Austria, produces from 1400 kg. of manganese ore only 50 kg. ferromanganese containing 35 per cent. manganese, so that of the manganese introduced into the furnace-charge only 4.5 per cent. is obtained in the metallic state. According to Blake (*ibid.* 54), the combination of the manganese with the iron is facilitated by a large addition of limestone (43 per cent. limestone to 57 per cent. manganese ore), whereby a slag is produced containing 25 per cent. manganous oxide and 33.5 per cent. lime. Ward, on the other hand, obtained in a charcoal blast-furnace 10.5 meters high, and having a tuyere 76 mm. wide, a ferromanganese containing 67.2 per cent. manganese, so that 58.1 per cent. of the manganese employed was obtained in the metallic state. The fuel used was a mixture of 1 pt. coke and 3 pts. charcoal, and the pressure of the blast was 0.28 on 1 c.c.

With regard to the use of manganese in iron metallurgy, Gautier is of opinion that the manganese acts as a reducing agent, removing iron oxide from the metallic iron, and preventing it from becoming 'hot short.' Henderson's process (vii. 699) yields a manganese-iron containing 25 to 75 per cent. of manganese. The amount of manganese required for reduction is usually 1 per cent., if added as manganese-iron. The resulting iron is extremely soft; its coefficient of elasticity is 22 to 25 kilos.; its resistance to strain, 45 kilos.; and its expansion, for 200 mm., 20 to 25 kilos. It does not become hard by tempering. The product of the resistance to strain multiplied by end-expansion is nearly 7 times that of ordinary iron, and more than twice that of hard steel. This iron is used in plating ships. Addition of $1\frac{1}{2}$ per cent. of manganese to inferior iron counteracts the influence of phosphorus. Addition of 1 per cent. of manganese to cast steel gives it great resisting power (*Chem. Centralbl.* 1877, 204).

See also Troost & Hautefeuille (p. 1111).

Boride. A compound of manganese and boron in equivalent proportions (Mn^2B^2) is obtained by heating boric oxide with manganese carbide, Mn^2C . It forms small grey-violet crystals, which dissolve in acids, with evolution of hydrogen, and are but slowly attacked by gaseous hydrogen chloride at a low red heat. It decomposes water at 100° , alkaline liquids at a lower temperature. Moist mercuric chloride decomposes it in a few minutes, forming manganous chloride, boric oxide, and hydrochloric acid. It is also decomposed by moist mercuric cyanide (Troost & Hautefeuille, *Compt. rend.* lxxxi. 1263).

Chlorides. Nicklès in 1864, by passing gaseous hydrogen chloride into a well-cooled mixture of manganese dioxide with ethyl oxide, obtained a green, very unstable liquid to which he assigned the composition $MnCl^{4.12}(C^2H^5)^2O.2H^2O$ (vi. 804), and, according to W. W. Fisher (*Chem. Soc. J.* xxxiii. 409), the tetrachloride of manganese contained in this compound is also produced when either of the higher oxides of manganese, Mn^2O^3 , Mn^2O^4 , or MnO^2 , is dissolved in strong hydrochloric acid. The brown liquids thereby formed decompose spontaneously at ordinary temperatures, with evolution of chlorine and formation of manganous chloride, $MnCl^2$, and each of them, when diluted with water, yields a precipitate of hydrated manganese dioxide. The analysis of the precipitate thus formed, combined with estimations by the iodometric method of the quantity of loosely combined chlorine (*i.e.* chlorine in excess of that required to form $MnCl^2$), led to the conclusion that the ratio of the manganese precipitated from the solution by water to the loosely combined chlorine is 1 : 2, and consequently that the formula of the higher chloride is $MnCl^4$.

Pickering, on the other hand (*Chem. Soc. J.* xxxv. 661), infers from experiments made in a similar manner:

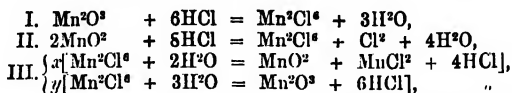
1. That when a solution of manganese dioxide in strong hydrochloric acid is diluted with water, a mixture of oxide is precipitated, which is not of definite composition, and that it may generally be represented by formulæ intermediate between $16MnO^2.5MnO$ and $36MnO^2.5MnO$.

2. That the manganese contained in this precipitate as dioxide bears to the loosely combined chlorine of the higher chloride from which it is precipitated the ratio of 1 : 2 atoms, and consequently that the total manganese precipitated bears to this chlorine the ratio of about 1 : 1.64 atoms.

3. That when the dioxide is dissolved in weaker acids, the amount of the higher chloride formed is not appreciably diminished.

4. That an increase in the actual amount of the aqueous acid employed for the solution is prejudicial to the stability of the higher chloride formed.

5. That the higher chloride formed in this reaction is Mn^2Cl^6 , and not MnCl^4 , the solution of the dioxide and sesquioxide by hydrochloric acid, and the subsequent decomposition of the sesquichloride formed, being represented by the following equations:



the reactions thereby represented taking place simultaneously, but in various proportions, and the average values for x and y being about 4 and 1 respectively.

Oxides. *Manganous Oxide*, MnO , occurs native in a manganiferous dolomite at Langbanshyttan, Wermaland, in small shining irregular lumps, green by reflected, red by transmitted light; they contain 98 per cent. MnO , the remainder being converted into manganite (Blomstrand, *Deut. Chem. Ges. Ber.* viii. 120).

Manganic Hydroxide occurs mixed with franklinite in pseudomorphs after calcite (locality not stated):

H^2O	Mn^2O^3	Fe^2O^3 (%)	ZnO	CaO	MgO	$\text{K}^2\text{O}, \text{Na}^2\text{O}$	CO^2	SiO^2
11.293	58.387	14.627	5.285	4.739	1.253	traces	3.488	0.170 = 99.242.

(%) Other determinations gave 12.777 and 16.129 per cent.

Dioxide, MnO^2 .—This oxide in the anhydrous state is usually regarded as an indifferent oxide. Frémy, however (*Compt. rend.* lxxiii. 1231), from an examination of its behaviour with acids and bases, infers that it behaves sometimes like a saline oxide, sometimes as an acid, sometimes as a base. Its resemblance to a saline oxide is seen in its reaction with melting potash, by which it is converted into potassium manganate and manganous hydroxide:



This formation of potassium manganate, without addition of oxygen from without or evolution of hydrogen, is characteristic of the dioxide, and serves to distinguish it from the other oxides of manganese, which yield manganates only under the influence of oxidising agents. The acid character of the dioxide is shown by its uniting with bases, forming compounds like those obtained by Weldon, viz. Ca.MnO^3 or CaO.MnO^2 , and $\text{CaH}^2.2\text{MnO}^3$ or $\text{CaO.H}^2\text{O}.2\text{MnO}^2$ (*Jahresb. f. Chem.* 1874, 1098). Its *basic* character has been especially studied by Frémy, who has succeeded, though with difficulty, in converting it into a *sulphate*, $\text{MnO}^2.2\text{SO}^3$, by acting on its hydrate with strong sulphuric acid. A better mode of preparing this salt consists in decomposing potassium permanganate with a considerable excess of sulphuric acid. 100 grams of permanganate are treated with a cold mixture of 500 grams of sulphuric acid and 150 grams of water, whereupon an oily layer of permanganic acid separates, which gradually decomposing, forms, at the end of a few days, a deep yellow liquid from which crystals can be obtained.

This salt, which Frémy at first regarded as a sulphate of the sesquioxide, is deliquescent, soluble in sulphuric acid, and decomposed by water, forming at the same time a hydrate of the dioxide, $\text{MnO}^2.2\text{H}^2\text{O}$. The liquor resulting from this decomposition contains no manganese. The yellow solution, exposed to the air or saturated with potassium sulphate, deposits a black basic sulphate, $\text{MnO}^2.\text{SO}^3$, which when redissolved in sulphuric acid reproduces the yellow sulphate. Certain salts, such as manganous sulphate, potassium sulphate, &c., combine with the yellow sulphate, forming well-crystallised double salts. The salt $\text{MnO}^2.\text{MnO}^2.(\text{SO}^3)^2 + 9\text{H}^2\text{O}$ separates in hexagonal plates on adding a strong solution of manganous sulphate to a solution of the salt $\text{MnO}^2.2\text{SO}^3$ in a large excess of sulphuric acid. It dissolves in dilute sulphuric acid, forming a rose-coloured solution. The same compound is formed by the action of strong sulphuric acid on manganese dioxide, as shown by the red colour of the resulting solution; also by the cautious addition of reducing agents, such as alcohol, to the solution of the yellow sulphate. The double salt might of course be regarded as containing manganese sesquioxide; but the existence of a corresponding potassium salt, and the fact that when decomposed by an alkali it gives a precipitate from which ammonia dissolves manganous oxide, leaving a residue of dioxide, are sufficient to show that the manganese exists in the salt in two different states of oxidation. Manganese sesquioxide is not broken up by the action of ammonia.

Regeneration.—A description of Weldon's process for the recovery of the dioxide from the residue of the chlorine manufacture is given in *Dingl. pol. J.* cxxix. 54; *Chem. Soc. J.* xxxiv. 938).

On the precipitation of Manganese as Dioxide, see pp. 1265, 1266.

A black *hydrated dioxide*, $3\text{MnO} \cdot 2\text{H}_2\text{O}$, which appears to have been previously observed by Berthier and Dingler, separates on gradually adding water to a mixture of potassium permanganate with strong sulphuric acid (Rammelsberg, *Deut. Chem. Ges. Ber.* viii. 232).

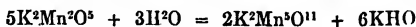
Manganates.—The preparation of barium manganate of fine green colour for use as a pigment is described by Böttger (*N. Rep. Pharm.* xxv. 115). See BARYTAGREEN, p. 151 of this Supplement.

Permanganate of Potassium.—According to Brücke (*Zeitschr. anal. Chem.* 1877, 231), the absorption-spectrum of this salt in dilute solutions exhibits five distinct bands, the first near D, the last near F, and the middle ones between E and b.

Potassium permanganate, when heated to redness, gives off oxygen and is converted into a salt having the composition $\text{K}^2\text{Mn}^2\text{O}^5$:



This compound is a brown-black powder, which is resolved by water into free potash and an acid salt:



(Rammelsberg, *loc. cit.*)

On the use of Potassium Permanganate as a disinfectant, see Schröter (*Dingl. pol. J.* cccix. 375; *Jahresh. f. Chem.* 1876, 1128).

On *Manganese Phosphates*, see PHOSPHATES.

Silicate. Rhodonite from a vein of crystalline limestone at Beloc near Husinec in the Bohemian Forest is described by Helmhaecker (*Min. Mitth.* 1873, 278).

On *Bustamile*, from Rezbanya in Hungary, see p. 354 of this volume; on *Jeffersonite* from Franklin, New Jersey, see vii. 709.

Sulphide. Anhydrous manganous sulphide, MnS , may be prepared by boiling a solution of a manganous salt with potassium oxalate, then adding ammonia and ammonium sulphide. The presence of sal-ammoniac does not interfere with the reaction (*Zeitschr. anal. Chem.* 1877, 319).

MANGANESE-GARNET. This mineral occurs, together with otrelite, at Salm-Château, near Ottrez in Belgium, in dodecahedrons ∞ O, a millimeter in size, containing, together with manganese and aluminium, only 4.49 per cent. FeO , and 1.9 per cent. Fe^2O^3 (L. de Koninck, *Jahrb. f. Min.* 1873, 163, 219).

MANGANESE-TANTALITE. See TANTALATES.

MANNITOL, $\text{C}^6\text{H}^{14}\text{O}^6$. *Mannite*.—According to Müntz (*Compt. rend.* lxxvi. 649; lxxxii. 210), this substance occurs, together with glucose and trehalose, in the higher kinds of fungi; some species, as *Agaricus muscarius*, contain only trehalose; in others, again, as *Agaricus campestris*, mannitol is the only kind of sugar present. Mannitol is also found in the alcoholic extract of the sugar-cane, and appears to be formed in the plant, together with a reducing, optically inactive sugar, by the action of vegetable organisms on cane-sugar.

On the relations of Mannitol to Polarised Light, see LIGHT (pp. 1216, 1221).

On the Schizomycetiv: Fermentation of Mannitol, see FERMENTATION (p. 777).

On the Heat of Formation of Nitromannitol, see HEAT (p. 973).

Mannitan, $\text{C}^6\text{H}^{10}\text{O}^4$, may be prepared by heating mannitol for an hour or two in an oil-bath to 295° with half its weight of water, the conversion being complete; also by heating mannitol to 120° with half its weight of strong sulphuric acid, saturating with barium carbonate, exhausting with alcohol, and evaporating. Its production in this manner depends on simple dehydration, and not on the decomposition of previously formed mannito-sulphonic acid. The decomposition of barium mannito-sulphonate by water is, indeed, never complete, a fact which may be due to the occurrence of an isomeric compound. Mannitan, heated for a considerable time with dilute sulphuric acid or baryta-water, does not yield any perceptible quantity of mannitol. The specific rotatory power of mannitan for the transition-tint is $[\alpha]_D = +36.5^\circ$.

Nitromannitan, $\text{C}^6\text{H}^8(\text{NO}^2)\text{O}^4$, is obtained by adding 1 pt. mannitan to a mixture of 10 pts. sulphuric acid (of 60° Bm.) and $4\frac{1}{2}$ pts. nitric acid (sp. gr. 1.5), leaving the mixture at rest, and keeping it cool; then throwing it into a large quantity of water, dissolving the deposit in ether, and leaving the ether to evaporate. In ether-alcoholic solution it exhibits a rotatory power $[\alpha]_D = +53.26^\circ$. By boiling alkalis it is converted into a blackish, gummy, non-explosive mass; by ammonium sulphhydrate into mannitan (Vignon, *Ann. Chim. Phys.* [5], ii. 433).

* The termination 'ol' is now applied to all compounds of alcoholic character (see NOMENCLATURE).

Mannitone, $C^6H^{12}O^8$, is produced by heating mannitol with water for three hours to 180° , whereby there is obtained, together with brownish products of decomposition, a viscid mass which may be easily separated from undecomposed mannitol by solution in alcohol. By purifying this solution with animal charcoal, evaporating, drying the remaining liquid at 120° , and leaving the resulting syrup to itself, small crystals are obtained, which must from time to time be separated from the soluble mother-liquor by means of alcohol, and finally purified by dissolving them in water, decolorising the solution with animal charcoal, and evaporating to the crystallising point. Mannitone does not reduce copper-solution; it has a sweet taste, and a rotatory power $[\alpha]_D = -25^\circ$. By heating to 295° it is converted into mannitan.

The syrupy mother-liquor, which no longer deposits crystals, yields, by repeated solution in alcohol, filtration through animal charcoal, evaporation, and finally heating to 120° , a light brownish viscid mass which does not yield either mannitol or mannitan when boiled with sulphuric acid or baryta-water. It forms a sulphonic acid whose barium salt is easily soluble; with nitric acid, a product resembling nitromannitan; and when heated to 295° is converted into mannitan. It tastes bitter-sweet, does not exert a reducing action, is not fermentable, is levogyrate: $[\alpha]_D = -5.59$. It has the composition $C^{12}H^{20}O^{21} - 2C^6H^{14}O^6 - H_2O$, and is, therefore, the ether of mannitol (Vignon, *loc. cit.*)

Mannitic Ethers containing Acid Radicles. It has already been mentioned (p. 1223) that the several mannitic ethers prepared from glucose and from invert-sugar have the same rotatory powers as the corresponding derivatives of mannitol from the ash-tree. The hexaceto-derivative of glucose-mannitol has, moreover, the same crystalline form as the corresponding ether of ash-mannitol, being orthorhombic, with a prismatic angle of $75^\circ 40'$, while that of the ash-mannitol ether is $73^\circ 45'$; the angle between the dome-faces (012) is $78^\circ 40'$ in the former, $78^\circ 30'$ in the latter; and the angle between prism and dome is $112^\circ 2'$ in the former, $112^\circ 10'$ in the latter. The mannitol obtained from the β -glucose of milk-sugar appears also to be identical with that from the ash (Bouchardat, *Compt. rend.* lxxxiv. 34).

MARGAROLIC ACID, syn. with ELZOMARGARIC ACID (p. 706).

MARMATITE, Zn^2FeS^4 , is found in quartz in the iron mines of Rio and Tarre della Marina, Elba, crystallised in cubes in combination with the tetrahedron, the cubic faces being rough, and the tetrahedral faces smooth. The exterior of the crystals has a dull brown to black colour, whilst the interior is reddish-brown with a metallic lustre. Streak reddish. Hardness = 4. Sp. gr. = 3.92 (G. Roster, *Jahrb. f. Min.* 1877, 531).

MATECERIC ACID. An acid obtained from the wax of the Yerba Maté (*Ilex paraguayensis*). When the solution obtained by exhausting the leaves of this plant with ether, or better with ether-alcohol, is treated with lime, then filtered and evaporated, a waxy residue is left, which may be freed from chlorophyll by treating its ethereal solution with animal charcoal. This solution, agitated with water to remove caffeine and other substances, and evaporated, leaves the pure waxy matter, which, when boiled with aqueous potash, partly dissolves, leaving a residue soluble in ether, much more butyraceous than the original substance, and separable by treatment with alcohol into an insoluble yellow transparent substance, and a soluble portion which is white and melts at 55° . On neutralising with hydrochloric acid the alkaline solution obtained by saponification of the wax, mateceric acid is obtained as a white precipitate which has acid properties, and is soluble in ether and in boiling alcohol. It melts at 105° – 110° , and has a density of 0.8151 at 26° . From the results of its analysis, it does not appear to belong to the acetic series, but its molecular weight is very high (Arata, *Gazz. chim. ital.* 1877, 366).

MATICO-STEAROPTENE. This substance separates from the volatile oil of matico when cooled to a few degrees below 0° , in crystals 2 cm. long and 5 mm. thick, belonging to the trapezo-tetartohedral division of the hexagonal system, and having the axial ratio $a : c = 1 : 0.31605$. It melts at 103° . The crystals exhibit a weak negative double refraction. Indices of refraction:

for the Lithium line:	extraordinary ray	=	1.5404,	ordinary ray	=	1.5415
" Sodium "	"	=	1.5436	"	=	1.5447
" Thallium "	"	=	1.5476	"	=	1.5488

Respecting the optical, rotatory power, see p. 1218.

MAXITE. To decide the question as to the identity or non-identity of this mineral from Sardinia with the Scotch leadhillite (p. 1171), Laspeyres (*J. p. Chem.* [2], xiii. 370; xv. 317) has made fresh analyses of both these minerals. The result of these analyses is to establish for leadhillite (A) and maxite (B) the same

chemical composition, represented by the formula $\text{H}^{10}\text{Pb}^{18}\text{C}^8\text{S}^5\text{O}^{36}$, or $5\text{PbSO}_4, 9\text{PbCO}_3, 4\text{PbO}, 5\text{H}_2\text{O}$, so that the name *marite* may be abandoned, but at the same time the received formula for leadhillite (vii. 732) must be considerably altered. The whole of the water is given off at once between 250° and 290° :

	H_2O	CO^2	SO^2	PbO
A (found) . .	1.818	7.981	8.424	81.777 = 100
B (found) . .	1.866	8.032	8.123	81.979 = 100
C (calc.) . .	1.838	8.083	8.171	81.908 = 100

Laspeyres (*Zeitschr. f. Kryst.* i. 194) has further established, by exact measurements, the crystallographic identity of the Scotch and Sardinian minerals, but refers them, not to the rhombic system, as Descloizeaux does, but to the monoclinic system, with the following fundamental angles and ratios:

$$\text{Angle } \frac{1}{2}\text{R}\infty : \infty\text{R}\infty = 42^\circ 4' 26''; \frac{1}{2}\text{P}\infty : -\text{P} - = 69^\circ 15' 27'';$$

$$-\text{P} : \infty\text{R}\infty = 36^\circ 7' 54''$$

$$\begin{array}{ccc} a : & b : & c \\ 1.7464 : & 1 : & 2.21545 \\ 1 : & 0.57220 : & 1.26768 \end{array}$$

or

The following faces were observed, and, for the sake of comparison with former statements, are given both as rhombic and as monoclinic forms:

rhomb. : $\infty\text{P}\infty, \infty\text{P}\infty$ (new), $\infty\text{P}, \infty\text{P}2$ (new), $\frac{1}{2}\text{P}\infty, \frac{3}{4}\text{P}\infty, 0\text{P}$
 monoc. : $\infty\text{P}\infty, \infty\text{R}\infty$ (new), $\infty\text{P}, \infty\text{P}2$ (new), $\frac{1}{2}\text{R}\infty, \frac{3}{4}\text{R}\infty, 0\text{P}$.
 rhomb. : $\text{P}, \frac{1}{2}\text{P}, \frac{3}{4}\text{P}\frac{7}{4}$ (new), $\text{P}\frac{3}{4}$ (new), $\text{P}2, \text{P}4, \frac{3}{4}\text{P}\infty$ (new)
 monoc. : $-\text{P}, +\frac{1}{2}\text{P}, +\frac{3}{4}\text{P}\frac{7}{4}$ (new), $+ \text{P}\frac{3}{4}$ (new), $\pm\text{P}2, \pm\text{P}4, -\frac{3}{4}\text{P}\infty$ (new).

The results of the optical investigation are as follows: Plane of optic axes normal to the plane of symmetry; the first (negative) median line is in the plane of symmetry in the obtuse axial angle, and forms with the vertical axis an angle of $0^\circ 12' 22''$. Dispersion of the axes rather large; $\nu > \rho$; a horizontal dispersion of the median lines was either non-existent or but very indistinctly observed (comp. Hinz, p. 1171).

MECONIC ACID, CHO. This acid is found in small quantity, together with morphine and narcotine, in officinal poppy-heads (G. Krause, *Arch. Pharm.* [3], v. 507).

The crystalline form of meconic acid is very much like that of α -pimelic acid (*q.v.*), both crystallising in transparent plates belonging to the orthorhombic system, and produced by predominant development of 0P . The crystals of meconic acid exhibit also the faces $\text{P}\infty, \text{P}\infty$, and ∞P : those of pimelic acid the faces $\infty\text{P}\infty$ and $\infty\text{P}\infty$. Pimelic acid is easily distinguished from meconic acid by the absence of the domes (C. A. Burghardt, *Chem. Soc. J.* [2], xii. 937).

Meconic acid, treated with phosphorus oxychloride, gives off carbon dioxide, and forms a derivative of comenic acid not yet investigated (H. Schiff, *Liebig's Annalen*, clxxii. 359).

The blood-red colour which meconic acid produces with ferric salts is much weakened by oxalic acid, ordinary phosphoric acid, and still more by metaphosphoric acid—a point which may be of importance in chemico-legal investigations (A. Dupré, *Chem. News*, xxxii. 15).

MECONIN. See NARCOTINE-DERIVATIVES.

MEDULLOSE. See PARENCHYMA.

MEERSCHAUM. A fibrous meerschaum (*sepiolite*) occurring in a silver mine of Utah, in veins $\frac{1}{2}$ cm. thick, partly white, partly bluish-green, has been analysed by A. Chester (*Sill. Am. J.* [3], xiii. 296), who assigns to it the formula $\text{Mg}^2\text{Si}^2\text{O}^8 + 2\text{H}_2\text{O}$ or $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

1. Mean of four analyses of the white variety. 2. Blue-green variety:

	SiO^2	Al^2O^3	Fe^2O^3	Mn^2O^3	CuO	MgO	$\text{H}_2\text{O}^{\text{(*)}}$	$\text{H}_2\text{O}^{\text{(?)}}$
1.	52.97	0.86	9.70	3.14	0.87	22.50	9.90	8.80
2.	50.15	2.06	1.02	2.09	6.82 (?)	18.29	9.30	10.32

(*) At 100° . (?) A small quantity at 200° , the rest at a strong red heat. (?) This large amount of copper is probably the cause of the blue coloration.

MEGARRHIZA. The root of *Megarrhiza californica* contains an organic acid, megarrhizic acid, a crystallisable resin, megarrhizitin, and a glucoside, megarrhizin, which may be split up by acids or by baryta-water into sugar and megarrhizioretin. The ash of the root contains magnesia, lime, iron oxide, potash, soda, chlorine, sulphuric, phosphoric, and silicic acid (J. P. Heaney, *Pharm. J. Trans.* [3], vii. 393).

MEJONITE. G. vom Rath (*Pogg. Ann. Ergänzbd.* vi. 381) describes, as analogous to the leucites which are encrusted with sanidin, a crystal of mejonite 5 cm. long and 2 cm. thick, imbedded in a block ejected from Vesuvius, the surface of which appears roughened and rounded by a mixture of sanidin and sodalite.

A carefully selected specimen of mejonite (sp. gr. 2.716 at 16°) from Vesuvius, analysed by E. F. Newman (*Jahrb. f. Min.* 1875, 747; 1877, 942), yielded the following numbers:

SiO ^a	Al ^a O ^a	CaO	MgO	Na ^a O	K ^a O	H ^a O	Cl	CO ^a
13.36	32.09	21.45	0.31	1.35	0.76	0.27	0.14	0.72 = 100.45.

Regarding the water, chlorine, and carbon dioxide as unessential, this analysis may be represented by the formula $\text{Na}_2\text{O}, 14\text{CaO}, 11\text{Al}_2\text{O}_3, 26\text{SiO}_2, 2\text{H}_2\text{O}$, which may, perhaps, also be written in the form $27(\text{CaO}, 5\text{Al}_2\text{O}_3, 10\text{SiO}_2) + (\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2, 2\text{H}_2\text{O})$.

MELAM. Volhard (*J. pr. Chem.* [2], ix. 28) regard's Liebig's melam (iii. 865) as probably a decomposition-product of guanidine thiocyanate, having the composition $\text{C}^3\text{N}^4\text{H}^4 = \text{CNS.CN}^2\text{H}^2 - \text{H}^2\text{S}$, that is to say, as a polymeric cyanamide, with which, in fact, the formula generally assigned to melam agrees very nearly.

When the residue left after prolonged calcination of melam at a high temperature, till gas is no longer given off, is fused with potassium carbonate, it yields nearly pure potassium mellonide, which may easily be obtained quite pure by treatment with a small quantity of acetic acid. A solution of the same residue in hot strong potash- or soda-ley immediately yields very fine crystals of cyameluric acid (Volhard).

When crude melam is dissolved in hot concentrated sulphuric acid, and alcohol is added to the solution, a snow-white chalky precipitate is formed, having the composition $\text{C}^3\text{H}^4\text{N}^4\text{O}^2$, and identical with ammelide obtained from urea. The *nitrate* of this base crystallises in scales, the *hydrochloride* in microscopic needles (S. Gabriel, *Deut. Chem. Ges. Ber.* viii. 1165).

Melam treated with strong sulphuric acid at ordinary temperatures yields melamine sulphate containing a quantity of melamine equal to 17 per cent. of the melam; ammeline is formed at the same time; at higher temperatures, the product consists of ammelide in nearly theoretical quantity, as found by Gabriel (*J. Jäger, Deut. Chem. Ges. Ber.* ix. 1554).

MELAMINE or **CYANURAMIDE**, $\text{C}^3\text{H}^3\text{N}^3 = \text{C}^3\text{N}^3(\text{NH}^2)^3$. The following methods of preparing this base are recommended by Claus a. Henn (*Liebig's Annalen*, clxxix. 120). A mixture of 25 grams melam, 100 grams potassium hydroxide, and $2\frac{1}{2}$ litres of water, boiled together for twenty hours, yields nearly 50 per cent. of melamine; and a mixture of 35–36 per cent. melam, 100 KHO and 1 litre of water boiled for six or seven hours yields 35–36 per cent. melamine. *Melamine hydriodide* crystallises in needles having a silky lustre (Claus a. Henn). *Melamine thiocyanate* is formed, together with melam, when ammonium thiocyanate is quickly heated to 250°, and this temperature is kept up till the mass solidifies. It dissolves in water and in alcohol, crystallises in prisms, and sublimates when cautiously heated.

Benzoyl-melamine, $\text{C}^3\text{N}^3\text{H}^3(\text{C}^7\text{H}^5\text{O}) = (\text{CN})^3 \begin{Bmatrix} \text{NH}^2 \\ \text{NH}^2 \\ \text{NH}(\text{C}^7\text{H}^5\text{O}) \end{Bmatrix}$, appears to be

formed, together with benzonitril, by the action of benzoyl chloride on cyanamide; it is a white substance easily soluble in water, and in acetic, nitric, and hydrochloric acids (C. Gerlich, *J. pr. Chem.* [2], xiii. 270).

A *polymeric benzoyl-melamine*, $(\text{CN.NH.C}^7\text{H}^5\text{O})^n$, called by Gerlich tribenzoyl-melamine, is formed, together with benzoyl-cyanamide, cyanamide, benzonitril, and carbon dioxide, by the action of an ethereal solution of benzoyl chloride on sodium cyanamide suspended in ether. The mass must at first be kept cool, afterwards heated for several days on the water-bath, or better, for some hours in a sealed tube at 100°, and the ethereal solution finally separated from a yellow mass containing sodium chloride. The solution heated for eight hours to 150° in a sealed tube and then quickly cooled, deposits small round crystalline groups of benzoyl-cyanamide and a white amorphous substance. The ethereal solution saturated with hydrochloric acid yields a precipitate having the composition $\text{C}^3\text{H}^3\text{N}^3\text{OCl}^2$.

The yellow mass insoluble in ether contains sodium chloride and tribenzoyl-melamine in the form of a yellow powder insoluble in water and in alcohol, soluble in phenol and in sulphuric acid, melting, with decomposition at 275°. When heated with water it takes up the elements of the latter, and is resolved into ammonia and benzoic acid. By distillation in a stream of hydrogen it is resolved into carbon dioxide, hydrogen cyanide, benzonitril, dibenzoyl-dicyanamide (m. p. 112°; easily soluble in alcohol, less easily in ether and in water), and pseudotriphenylmelamine.

This last compound, isomeric with Hofmann's triphenylmelamine (p. 1271) does not melt at 360°. It forms shining yellow prisms, which are most readily purified

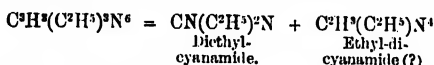
by dissolving them in phenol, and mixing the solution with alcohol (Gerlich, *loc. cit.*)

Trimethyl-melamine, $C^3H^3(CH^3)^3N^3 = (CN)^3N^3H^3(CH^3)^3$ (A. W. Hofmann, *Deut. Chem. Ges. Ber.* iii. 264). This base is prepared, similarly to triethyl-melamine (vi. 808, 1050), by desulphuration of methyl-thiocarbamide, the first product of this reaction being probably methyl-cyanamide, $N^2(CS)H^3(CH^3) - H^3S = N(CN)H(CH^3)$, which is then converted by polymerisation into trimethyl-cyanuramide or trimethyl-melamine.

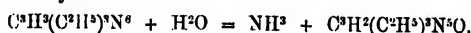
Trimethyl-melamine crystallises from water or alcohol in small colourless prisms having a strong alkaline reaction; volatilises when heated, without previous fusion; and is decomposed by hydrochloric acid, with separation of ammonia. Its *platinochloride*, $C^3H^3(CH^3)^3N^3 \cdot 2HCl.PtCl_4$, crystallises in laminae sparingly soluble in water and in alcohol.

Triamyl-melamine, $C^3H^3(C^5H^{11})^3N^3$, prepared in like manner, forms a strongly alkaline syrup, insoluble in water and in aqueous hydrochloric acid. Its *platinochloride*, $C^3H^3(C^5H^{11})^3N^3 \cdot 2HCl.PtCl_4$, forms a network of yellow crystals, soluble in water, slightly soluble in alcohol, and is decomposed by boiling with hydrochloric acid, with separation of ammonia.

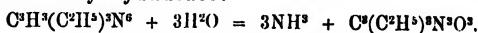
These trisubstituted melamines, as already observed, are not the direct products of the desulphuration of thiocarbamides, their formation being preceded by that of substituted cyanamides: in fact, the direct product of the desulphuration of ethyl-thiocarbamide does not crystallise, has no alkaline reaction, and does not yield a crystallisable platinum-salt; and it is only after repeated evaporation that complete polymerisation is effected. Moreover, Hofmann has given direct proof of the correctness of this view, by converting ethyl-cyanamide, prepared by the action of gaseous cyanogen chloride on ethylamine (ii. 190), into triethyl-melamine. He likewise explains the resolution of ethylecyanamide by heat into diethylecyanamide and a crystalline base, $C^2H^2(C^2H^5)^2N^3$ (*loc. cit.*) by a decomposition of triethylamine represented by the equation:



By brisk ebullition with *hydrochloric acid*, triethyl-melamine is resolved into ammonia and triethylammeline:



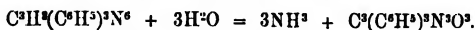
but by digestion for several hours with hydrochloric acid in sealed tubes it is converted into ammonia and methyl-cyanurate:



Similar reactions take place in the phenyl series.

Triphenyl-melamine, $C^3H^3(C^6H^5)^3N^3$ (Hofmann, *loc. cit.*) Monophenylthiocarbamide is converted by desulphuration into phenyl-cyanamide or cyananilide, agreeing in properties with that which Cahours & Cloez obtained by the action of gaseous cyanogen chloride on aniline (iv. 442). The product has at first the consistence of colophony, but may be crystallised by solution in alcohol and heating, or by leaving the alcoholic solution at rest for some time at ordinary temperatures. It is very soluble in alcohol and ether, melts at $36^\circ - 37^\circ$, and when once fused takes a long time to solidify; it changes into triphenyl-melamine, slowly at ordinary temperatures, quickly when fused at the heat of the water-bath.

Triphenyl-melamine, when recrystallised from alcohol, forms pyramidal groups of prisms, melting at $162^\circ - 163^\circ$. It is insoluble in cold, very slightly soluble in boiling water, easily soluble in alcohol and ether, especially when warm, and crystallises from the hot solution in capillary needles. Its *platinochloride*, $C^3H^3(C^6H^5)^3N^3 \cdot 2HCl.PtCl_4$, is a yellow precipitate which crystallises well. The base is decomposed by boiling hydrochloric acid, with separation of ammonia; and its alcoholic solution heated to boiling for a short time with hydrochloric acid, deposits on cooling crystals of phenyl-cyanurate:



MELANGLANCE. This mineral, from Freiberg, was found by Frenzel (*Jahrb. f. Min.* 1874, 188) to contain 68.6% per cent. silver, 15.76 antimony, and 16.49 sulphur, agreeing with the formula $5Ag^2S.Sb^2S^3$, which requires 68.36 Ag, 15.44 Sb, and 16.49 S. Sp. gr. = 6.28 at 18° .

MELANILINE. This compound crystallises in elongated monoclinic prisms exhibiting the faces $\infty P\infty$, $\infty R\infty$, $-P\infty$, $+R\infty$, ∞P . No distinct cleavage (Arzruni, *Pogg. Ann.* clii. 284).

MELANOPHLOGITE. A mineral occurring on sulphur at Girgenti, in small light-brown cubes and cubic twins, closely intergrown with a crust of quartz, and mixed with sulphur, calcite, and cœlestine. The cubes when heated turn green, blue, and finally black-blue: hence the name of the mineral. Sp. gr. = 2.03–2.04; after ignition, 1.95. An analysis made with a very small quantity of material gave:

SiO ²	Fe ² O ³ , Al ² O ³	SrO	SO ²	H ² O	
86.29	0.7	2.8	7.2	2.86	= 99.85

Deducting the iron and strontia, the latter combined with 1.3 per cent. SO² as cœlestine, there remains, as essential constituents, only water, sulphuric acid, and silica. The mode of combination of the silicon and sulphur has not been made out (A. v. Lasaulx, *Jahrb. f. Min.* 1876, 250, 627). Further notices on this mineral have been published by v. Zephanovich (*ibid.* 627). A. Brezina (*Min. Mitth.* 1876, 243) calls attention to a Grecian mineral described by A. Guyard (*Bull. Soc. Chim.* [2], xxii. 61) under the name of *sulphuricin* or *silex sulphuricin*, which is impregnated with sulphur and free sulphuric acid, and was found to contain:

SO ²	S	H ² O	SiO ²	CaO	Al ² O ³	Fe ² O ³	MgO
6.80	4.10	6.10	80.38	1.25	0.43	8.57	0.37 = 100

Assuming that in this analysis, in which there is an excess of 8 per cent., the 8.57 Fe²O³ should be 0.57, the numbers will agree nearly with those in the analysis by v. Lasaulx.

MELANOSIDERITE is the name given by J. P. Cooke (*Jahrb. f. Min.* 1875, 651) to a black amorphous mineral from West Chester, Pennsylvania. The analysis by W. H. Melville indicates a highly basic silicate having the composition 4Fe²O³.SiO² + 6H²O. It might be regarded as an impure brown hematite, were it not for the gelatinising reaction which it exhibits. Sp. gr. = 3.390–3.392.

	SiO ²	Fe ² O ³	Al ² O ³	H ² O	
Analysis	7.42	75.13	4.34	13.83	= 100.72
Calculation	7.42	79.21		13.37	= 100

MELAPHYRE. A microscopic examination of melaphyres has been published by G. Haarmann (*Zeitschr. geol. Ges.* xxv. 436; *Jahrb. f. Min.* 1874, 313). The greater number of specimens exhibited, together with a vitreous ground-mass, plagioclase, less abundantly orthoclase, magnetic iron oxide, olivine (hitherto regarded as the most regular constituent of the melaphyres), augite (occurring less frequently than is commonly supposed), and apatite. Schillerspar, nephelin, and quartz were found in individual specimens, hornblende never. Among the varieties of structure exhibited, special mention must be made of a very distinct micro-faceted structure, inasmuch as it affords distinct evidence as to the genesis of the rock, pointing to its metamorphic formation from sedimentary material.

C. Doelter (*Jahrb. f. Min.* 1876, 563) has examined the mineralogical constitution of the melaphyres and augite-porphyrines of South Tyrol, which he divides into: 1. *Augite-melaphyres* (a. Augite-porphyry; b. Augite-melaphyres poor in augite, and augite-hornblende melaphyres). 2. *Hornblende melaphyres*. 3. *Melaphyres free from augite and hornblende*. The chief constituents of these melaphyres are plagioclase, orthoclase, augite (sometimes replaced by uraltite), hornblende, and magnetic iron oxide; subordinate: olivine and apatite; as secondary products: epidote, calcite, clefsite, chalcedony, and iron pyrites, as well as pseudomorphs after augite and olivine.

Metamelaphyre, Metadiabase, and Metadolerite. These terms are applied by J. D. Dana (*Sill. Am. J.* [3], xi. 119) to the rocks which constitute the heights forming the western boundary of the plain of New Haven. They are metamorphic formations probably of old Silurian age, but petrographically very nearly allied to eruptive dolerite, diabase, and melaphyre. The term *dolerite* is in this nomenclature not restricted, as usual, to eruptive rocks of the tertiary age, but denotes a rock free from chlorite, in opposition to the chloritic dialases. G. W. Hawes (*ibid.* 122) has supplemented Dana's memoir by a series of analyses in which the composition of these metamorphic rocks is compared with that of the corresponding formations of eruptive material, in order to show the petrographico-chemical identity of the two classes.

1. *Metadolerite* from Stoekel's farm; crystallo-granular. The mineral constituents were found by calculation to consist of 55 per cent. augite, 41 labradorite, and 3 titanite iron.

2. *Dolerite* from West Rock, New Haven, an eruptive rock, added for comparison.

3. *Metadiabase* from the cutting of the Derby railway; light green, fine-grained variety, consisting, according to microscopical examination, of augite, chlorite, labra-

donite, and titanite iron. From the absence of calcium carbonate it is inferred that the chlorite has been formed simultaneously with the other constituents, not at the expense of the augite.

4. *Metadiabase*, to the south of Maltby Park; porphyritic from the presence of felspar, otherwise formed of the same constituents as the preceding. Whether anorthite likewise occurs cannot be decided, on account of the impurity of the felspar which was separated for analysis, but its occurrence is not improbable.

5. *Diabase, eruptive*, from Lake Saltontall.

6. *Metamelaphyre*, from Stoeckel's farm; crypto-crystalline. Calculation gave, as the component mineral species, 44 per cent. augite, 53 oligoclase, and 3 titanite iron.

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO	Na ² O	K ² O	TiO ²	H ² O
1.	50.36	14.57	2.48	8.31	0.46	11.13	7.62	3.04	0.44	1.70	0.78
2.	51.78	14.20	3.59	8.25	0.44	10.79	7.63	2.14	0.39	—	0.63
3.	48.20	14.12	2.00	7.41	1.24	11.50	8.19	2.60	0.23	1.58	2.20
4.	48.61	17.81	0.25	8.46	0.20	11.16	7.76	2.77	0.47	1.35	1.63
5.	49.28	15.92	1.91	10.20	0.37	7.44	5.99	3.40	0.72	—	3.90
6.	55.07	14.18	7.20	1.92	0.30	9.03	5.98	4.11	0.37	1.56	0.72

In 1. traces of Cr; in 2. 0.14 per cent. P₂O₅; in 5. 1.14 CO₂. Totals, 1. = 100.89; 2. = 99.89; 3. = 99.27; 4. = 100.47; 5. = 100.27; 6. = 100.44. Sp. gr. 1. = 3.04; 2. = 3.03; 4. = 3.01; 5. = 2.86; 6. = 2.99.

The rocks of New Hampshire have also been discussed in the same manner by G. W. Hawes (*Sill. Am. J.* [3], xii. 129).

1. *Hornblende* from the *metadiorite* of North Lisbon. The rocks may be regarded, according to their amount of silica, as *Oligoclase-* and *Labrador-metadiorite*.

2. *Metadiabase* from Littleton.

3. *Metadiabase* containing hornblende, together with augite and chlorite. Nos. 2 and 3 exhibit structures which are regarded by Hawes as organisms.

4. *Metadiabase slate* from Hanover, analysed by Pease.

5. *Metadolerite* from Littleton, containing hornblende, apparently formed from augite.

6. *Clay-slate* from Woodrill; wrinkled and exhibiting only traces of crystalline constituents: 'nevertheless it has a composition which would have afforded a good granite if circumstances had been favourable to the formation of that rock.'

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO	K ² O	Na ² O	TiO ²	H ² O
1.	49.03	13.72	—	9.84	0.40	11.22	11.96	—	2.40	—	0.90
2.	45.56	16.57	0.36	9.40	0.20	8.01	10.34	1.20	2.55	1.20	3.93
3.	48.79	16.97	1.69	8.97	0.20	9.98	6.98	—	3.30	1.10	2.65
4.	46.65	19.26	2.58	9.73	0.25	9.07	6.67	0.09	3.31	0.52	2.39
5.	40.25	13.62	5.46	10.36	—	10.31	8.86	0.59	1.96	6.53	0.74
6.	60.49	19.35	0.48	5.98	—	1.08	2.89	3.44	2.55	—	3.66

In 2. 1.02 per cent. CO₂.

Totals: 1. = 99.47; 2. = 100.34; 3. = 100.63; 4. = 100.42; 5. = 98.68; 6. = 99.92.

Sp. gr. 2. = 2.96; 3. = 2.96; 4. = 3.03.

Peculiarly formed conglomerates from South African melaphyres are described by E. Cohen (*Jahrb. f. Min.* 1875, 113). One of these rocks from the Malati mountains exhibits conglomerates consisting of heulandite (p. 1030), in peculiar ramifications resembling certain precious corals. In the second rock, from Backhaus on the left bank of the Vaal, are imbedded tubes more than 10 cm. long, and having a maximum diameter of 1 cm., which gradually renew themselves, and are filled with chalcedony coated with delessite. The loose cylinders of chalcedony (so-called 'pipe-stones'), which are of frequent occurrence in the diamond-washings, are attributed by Cohen to conglomerates of this kind which have fallen out of the rock.

MELEZITOSE. See SUGARS.

MELILOT. The yellow melilot (*Melilotus officinalis*), at flowering time, yields by distillation with steam 0.2 per cent. of melilotol, an acid oil, to which the odour of the flowering plant is due. This oil is slightly soluble in water, easily in alcohol and ether, and is easily converted into melilotic acid (T. L. Phipson, *Chem. News*, xxxii. 25).

MELINOPHANE. Crystals of this mineral have been measured by E. Bertrand (*Compt. rend.* lxxiii. 711), who refers them to the quadratic system, indicating the faces P and P_∞, whereas hitherto rhombic forms have been assumed with ∞P = 91°. The faces hitherto regarded as produced by cleavage parallel to OP are,

according to Bertrand, not cleavage-faces at all, inasmuch as the crystals exhibit no indication of cleavability.

MELISSIC ACID, $C^{30}H^{40}O^2$. This acid and its salts have recently been investigated by L. v. Pievorling (*Liebig's Annalen*, clxxxiii. 344). The acid is prepared by heating myricylalcohol, $C^{30}H^{40}O$, to 220° , with three times its weight of potash-lime in a tube open at one end, the process being continued as long as hydrogen is given off, and the contents of the tube finally treated with hydrochloric acid. The crude melissic acid thereby separated is dissolved in alcohol and precipitated with lead acetate; the precipitate is washed with hot alcohol; and the melissic acid separated from it by digestion with alcohol containing hydrochloric acid, is purified by recrystallisation from alcohol.

Melissic acid thus prepared forms shining silky scales appearing under the microscope to be made up of slender needles, and melting at 88.5° . It is slightly soluble in ether, easily in boiling alcohol.

Lead melissate, $(C^{30}H^{38}O^2)^2Pb$, is insoluble in alcohol and in ether, but dissolves in boiling chloroform and toluene, and crystallises from the latter in yellowish needles.

Silver melissate, $C^{30}H^{38}O^2Ag$, forms white masses which quickly turn brown when exposed to light, melt to a black mass between 94° and 95° , and behave towards solvents like the lead salt. The *copper salt* is a green powder. The *potassium salt* dissolves in 20 parts water, and crystallises from alcohol in white needles, from ether in scales.

Ethyl melissate, $C^{30}H^{38}O^2.C^2H^5$, prepared from the silver salt with ethyl iodide, is a white waxy mass, melting at 73° . *Amyl melissate*, $C^{30}H^{38}O^2.C^5H^{11}$, may be prepared by passing hydrogen chloride into a solution of the acid in amyl alcohol, and when purified by crystallisation from ether, forms white shining needles, melting at 69° , resolidifying at 67° , soluble in alcohol, ether, benzene, and chloroform.

MELISSYL ALCOHOL. See MYRICYL ALCOHOL.

MELITOSE. See SUGARS.

MELLITIC ACID, $C^{12}H^6O^{12} = C^6(COOH^6)$. Claus a. Poppe (*Dent. Chem. Ges. Ber.* 1877, p. 559) find that pure mellitic acid may be prepared from very impure, earthy, nearly black honeyston., by evaporating the ammoniacal extract to dryness and heating the residue for some hours to 120° – 130° . The ammoniacal salts of the humus-acids are thereby decomposed and rendered insoluble, so that, on subsequently boiling the residue with water, a nearly colourless solution of mellitic acid is obtained.

Acid mellitates are obtained both by evaporating the solutions of the neutral salts, and by heating mellitic acid with metallic chlorides. With an ammoniacal magnesium-solution, moderately dilute solutions of mellitic acid yield a heavy crystalline precipitate of the salt $(NH^4)^2Mg^{+2}C^{12}O^{12} + 15H^2O$, which crystallises from hot water in large prisms having a vitreous lustre. A *magnesium-potassium* salt, which likewise crystallises well, is obtained in a similar manner. *Zinc-ethyl* acts on mellitic acid in the same manner as on oxalic acid.

Mellitic Hexchloride, $C^{12}O^6Cl^6$, is formed by the action of phosphorus pentachloride on mellitic acid, together with a number of secondary products, from which it may be freed by recrystallisation from ether. From this solvent and from benzene it crystallises very readily in hard vitreous prisms which melt at 290° , and sublime in laminae at about 240° . An *oxychloride*, $C^{12}C^6Cl^{12}$, has also been obtained (Claus a. Poppe).

Mellitic Ethers.—According to Busso a. Kraut (*Liebig's Annalen*, clxxvii. 272), the melting point of ethyl mellitate (73°) is lowered to 51.5° by admixture of small quantities of methyl mellitate. That of the latter is also lowered by the presence of small quantities of impurities.

The results of Baeyer's investigations on mellitic acid and its derivatives have already been given (vi. 808–814; vii. 784–785).

Trimellitic acid, $C^6H^2(CO^2H)^3$, is obtained by the oxidising action of potassium permanganate on xylic acid prepared from pseudocumene. This shows that trimellitic acid (as formerly suggested by Baeyer) has the same constitution as pseudocumene, viz. (1 : 2 : 4); and since trimesic acid has the position 1 : 3 : 5, there remains for hemimellitic acid only the position 1 : 2 : 3. The above reaction yields isophthalic as well as trimellitic acid (G. Krinos, *Dent. Chem. Ges. Ber.* x. 1491).

MELLONE. On the formation of potassium mellonide from the residue left after the calcination of mklam, see p. 1270.

MELONITE. See TELLURIUM MINERALS.

MENTHENE, $C^{10}H^{18}$. This hydrocarbon, obtained by distilling solid peppermint-camphor with zinc-chloride, is converted by the action of bromine into cymene, $C^{10}H^{18} + Br^2 = C^{10}H^{17} + 4HBr$, the hydrocarbon being first treated with a solution of

bromine in potassium bromide and the resulting addition-product distilled. A liquid compound having the same composition as solid peppermint camphor, likewise yielded menthene by distillation with zinc chloride (Beckett & Wright, *Chem. Soc. J.* xxix. 1).

MERCAPTAN and MERCAPTIDES (P. Claesson, *Bull. Soc. Chim.* [2], xxv. 183; *J. pr. Chem.* [2], xv. 193). Mercaptan, C^2H^5SH , may be advantageously prepared by neutralising a mixture of sulphuric acid and alcohol with sodium carbonate; evaporating; and after the sodium sulphate has crystallised out, mixing the mother-liquor with potassium sulphhydrate and gently heating the mixture for twelve hours in a retort, the vapours which escape condensation in the receiver being passed into a solution of caustic potash. By this process, 1 litre of alcohol and 350 grams of potassium hydrate yield 280–300 grams of crude mercaptan containing about 70–80 per cent. ethyl sulphhydrate, and 20–30 per cent. ethyl monosulphide. The product may be freed from hydrogen sulphide by repeated agitation with potash-ley, and the mercaptan separated from the ethyl sulphide by fractional distillation, or, better, by converting it into the sodium salt (*infra*), evaporating the alcoholic solution of this salt to dryness, adding water, and either filtering the solution, or agitating it with benzene or other hydrocarbons which dissolve the ethyl sulphide. The alkaline solution thus purified yields, on neutralisation with dilute sulphuric acid, perfectly pure mercaptan.

Mercaptan is a powerful reducing agent, converting, for example, nitrobenzene into azobenzene; the alkaline mercaptides exert a still more powerful reducing action.

A hydrate of mercaptan, $C^2H^5S \cdot 18H^2O$, first obtained by H. Müller (*Arch. Pharm.* [2], cl. 1:7), is formed when the vapours evolved in the preparation of mercaptan are passed through a condensing tube containing water cooled to 8° or a lower temperature, and solidifies to a crystalline mass of small needles which may be kept undecomposed for several days in a closed vessel at a temperature of 12° – 14° .

Mercaptides. The sodium and potassium compounds may be prepared either by dissolving the metal in mercaptan, whereupon the compound separates out in white snowy masses, or better, by dissolving potassium or sodium in absolute alcohol and adding mercaptan, drop by drop, or by passing mercaptan-vapour into the alcoholate. Sodium mercaptide, C^2H^5SNa , is decomposed by water into sodium hydrate and mercaptan, and by excess of alcohol into sodium alcoholate and mercaptan. The latter reaction, however, is by no means so complete. An aqueous solution of potash or soda dissolves mercaptan, partially converting it into mercaptide, and great contraction of the solution ensues. Sodium mercaptide absorbs oxygen when the gas is passed through its alcoholic solution, ethyl disulphide being formed. The action is different, however, when dry oxygen is passed over dry sodium mercaptide, oxidation then taking place, slowly at ordinary temperatures, more quickly at 100° – 120° , the change being complete when a solution of a small portion of the product in water gives with lead acetate, no longer a yellow, but a white precipitate. If the mass, which is not altered in appearance, be then dissolved in water, a small quantity of ethyl bisulphide separates out; and on removing this by filtration, mixing the filtrate with barium chloride, removing the small precipitate thereby produced (chiefly barium sulphate) by filtration, passing carbon dioxide into the filtrate, evaporating to dryness and exhausting with alcohol, a solution is obtained which, on evaporation, yields a neutral very deliquescent and indistinctly crystalline salt, exhibiting the composition and reactions of sodium ethylsulphinat, C^2H^5SOONa . With solutions of metallic salts, mercaptan and sodium-mercaptide act exactly like hydrogen sulphide and the sulphhydrates of the alkali-metals.

Thallium mercaptide, C^2H^5STl , prepared by agitating thallous carbonate with mercaptan, is a yellow curdy precipitate slightly soluble in water.

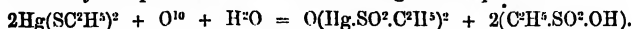
Ferrous mercaptide, $(C^2H^5S)_2Fe$ (?), is obtained by mixing an alcoholic solution of ferric chloride with mercaptan and ammonia, as a black slimy mass resolved by heating with water into mercaptan and ferrous hydrate.

Nickel mercaptide, $(C^2H^5S)_2Ni$, prepared in like manner, is a chocolate-brown powder not decomposed by hot water.

Cobalt mercaptide, $(C^2H^5S)_2Co$, is obtained by agitating mercaptan with cobalt acetate, as a gummy precipitate, which, unlike all other mercaptides, is not attacked even by fuming nitric acid.

The mercaptides of Zinc and Cadmium, $ZnS^2(C^2H^5)^2$ and $CdS^2(C^2H^5)^2$, are precipitated on adding mercaptan to their compounds with weak acids; they dissolve in dilute acids without decomposition, and are reprecipitated on neutralising the acid. They are white, indistinctly crystalline bodies, and are best prepared from the acetates. They dissolve in ammonia, and are reprecipitated on neutralisation.

Mercuric mercaptide is best prepared by shaking mercuric cyanide with mercaptan, and separates out in long very thin crystals. On application of heat it melts to an oil, devoid of smell and taste. On treating it with warm nitric acid, a basic mercuric ethylsulphonate is formed, according to the equation :



Mercaptides of the Platinum Metals.—Of the metals of this group, only platinum, palladium, and rhodium appear to be capable of forming mercaptides. The platinum salt has been already mentioned (ii. 549). *Palladium mercaptide* is a powder of a fine yellow colour, which decomposes, when heated, with a glimmering light, and evolution of heat sufficient to melt the palladium. *Rhodium mercaptide*, $\text{Rh}^2(\text{S}.\text{C}^2\text{H}^3)^6$, obtained from salts of rhodium sesquioxide, is a yellow precipitate.

The lower oxides of *iridium*, *ruthenium*, and *osmium* are not acted on by mercaptan ; the higher oxides are merely reduced. Claesson suggests that this difference of reaction might be utilised as a method of separating the platinum metals one from the other, especially for obtaining platinum absolutely free from iridium, and for separating small quantities of platinum from the osmium and iridium metals.

Tin mercaptides.—The *stannic salt*, $\text{Sn}(\text{S}.\text{C}^2\text{H}^3)^4$, is formed by the action of stannic chloride on mercaptan, both dissolved in carbon sulphide, and remains as a thick oil after the solvent has been removed by distillation ; it is also formed on adding mercaptan to a strong aqueous solution of stannic chloride. It remains liquid at -40° , and may be distilled in a vacuum without decomposition, but is decomposed by distillation under the ordinary pressure, with formation of ethyl sulphide and separation of metallic tin. *Stannous mercaptide*, $\text{Sn}(\text{S}.\text{C}^2\text{H}^3)^2$, is formed on adding mercaptan to a solution of stannous acetate, as a yellow precipitate, which oxidises very quickly on exposure to the air.

Bismuth mercaptide, $\text{Bi}(\text{S}.\text{C}^2\text{H}^3)^3$, one of the most characteristic salts of the group, is obtained by mixing a solution of a salt of bismuth with mercaptan, and crystallises in long flexible yellow needles, moderately soluble in alcohol and in ether. It melts at 79° , oxidises easily in air, and when strongly heated decomposes into the sulphides of bismuth and ethyl.

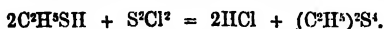
Arsenious mercaptides.—Arsenious chloride acts on mercaptan at ordinary temperatures, forming arsenious chlorodimercaptide, $\text{As}(\text{SC}^2\text{H}^3)^2\text{Cl}$, the substitution of SC^2H^3 for Cl not going any further even at 100° . The trimercaptide, $\text{As}(\text{SC}^2\text{H}^3)^3$, is best obtained by adding sodium mercaptide to an ethereal solution of arsenious chloride, keeping the latter in excess, and afterwards removing this excess by a stream of ammonia-gas. The product, after filtration and removal of the ether by distillation, is quite free from chlorine. Both these products are colourless fetid oils. The former when heated gives metallic arsenic, arsenic chloride, and ethyl disulphide ; the latter metallic arsenic and ethyl disulphide. The former reacts with water, giving arsenious acid, hydrochloric acid, and mercaptan, but is not oxidised by air ; while the latter is not acted on by water, but decomposes in air, with formation of arsenious acid.

Phosphorus trichloride and mercaptan do not react at low temperatures, but on heating the mixture, the three chlorine-atoms are successively replaced by the group SC^2H^3 , the replacement of the third chlorine-atom being, however, not completely effected till the substances are heated together at 100° in sealed tubes. The trimercaptide, $\text{P}(\text{SC}^2\text{H}^3)^3$, is a colourless fetid oil, resolved by distillation into phosphorus and ethyl disulphide, and slowly decomposed by water at ordinary temperatures.

Antimony trichloride unites directly with mercaptan, forming the compound $\text{SbCl}^3.\text{C}^2\text{H}^3\text{S}$, which remains, on evaporating over the water-bath, as an oil, which does not oxidise in the air, but is decomposed by water like antimonious chloride itself, the mercaptan being set free.

Carbon mercaptides are obtained by the action of sodium mercaptide on the carbon chlorides CCl^4 , C^2Cl^6 , and C^3Cl^8 . *Carbon tetramercaptide*, $\text{C}(\text{S}.\text{C}^2\text{H}^3)^4$, is a light yellow oil having a peculiar odour, a sp. gr. = 1.01, and decomposing when distilled. *Dicarbon-hexamercaptide*, $\text{C}^2(\text{S}.\text{C}^2\text{H}^3)^6$, is a heavy, nearly colourless, fetid oil, solidifying at very low temperatures. *Dicarbon-tetramercaptide*, obtained by heating carbon dichloride, C^2Cl^4 , with sodium mercaptide at 100° , crystallises in very fine rhombohedrons having a faint odour and melting at 54° . All these compounds are oxidised by nitric acid to carbonic and ethylsulphonic acids.

Sulphur Mercaptides or Ethyl Polysulphides.—The *tetrasulphide*, $(\text{C}^2\text{H}^3)_4\text{S}^4$, is formed by mixing the solutions of sulphur chloride and mercaptan in carbon sulphide :



After removal of carbon sulphide and excess of mercaptan by distillation, the tetra-sulphide remains as a light-coloured, very fetid oil, heavier than water, soluble in carbon sulphide and in ether, very sparingly in alcohol. It converts most metals into sulphides, potassium cyanide into the thiocyanate, potassium hydroxide into thio-sulphate. It is resolved by distillation into sulphur and the disulphide, $(C^2H^5)_2S^2$, by contact with water into sulphur and $(C^2H^5)_2S^3$. It dissolves sulphur at 156° , possibly forming the pentasulphide.

MERCAPTOIC ACIDS. This name has been given to the sulphuretted dyes, which Croissant and Bretonnière obtain by action of metallic sulphides, or of sulphur and an alkali, on carbohydrides, gum-resins, &c. (p. 698).

MERCURIALINE. According to E. Schmidt (*Deut. Chem. Ges. Ber.* x. 2226), this base, obtained from *Mercurialis perennis*, is identical with methylamine.

MERCURIPHENYLAMMONIUM CHLORIDE, $NH(C^6H^5)HgCl$, is formed, together with mercuridiphenylammonium chloride, on mixing the boiling solutions of aniline and mercuric chloride. The latter remains in solution, while the former separates as a yellowish precipitate. After repeated boiling with alcohol, it forms an amorphous insoluble 'phenylated white precipitate' (Carl Forster, *Deut. Chem. Ges. Ber.* vii. 294).

MERCURY. According to J. W. Mallet (*Proc. Roy. Soc.* xxvi. 71), the sp. gr. of solid mercury at its freezing point, -38.85° , is 14.1992, compared with water at 4° .

On the Specific Heat of Liquid Mercury, see HEAT (p. 928); of Mercury-vapour, p. 934.

On the Expansion of Mercury by Heat, see p. 935.

Heat-conductivity.—According to H. Herwig (*Pogg. Ann.* cli. 177), the heat-conductivity of pure mercury between the temperatures of 40° and 160° is perfectly constant, whereas its conducting power for electricity is known to vary with the temperature. Mercury, therefore, presents an exception to the law laid down by Wiedemann and Franz (*Pogg. Ann.* lxxxix. 497; *Jahresb. f. Chem.* 1853, 92), according to which the conduction of heat in metals is as variable as their power of conducting electricity. On the other hand, the result above mentioned relating to mercury agrees with Lorenz's law (*Pogg. Ann.* cxlvii. 429; *Jahresb.* 1872, 52), according to which the heat-conducting power is the same at all temperatures.

Electric Conductivity of Mercury-vapour.—Herwig (*Pogg. Ann.* cli. 350) finds that this vapour conducts electricity, not like a metal, but rather like a voltaic arc; moreover, it exhibits, like other gases, as shown by Hittorf (p. 726), a certain resistance to the transference of electricity at the cathode. Mercury-vapour at 400° in a tube 4 mm. in diameter, and between columns of liquid mercury as electrodes, exerts a resistance of about 50,000 Siemens' mercury-units.

Electric Impulsion.—Du Moncel's observations on the movement of a drop of mercury at the bottom of a layer of water through which an electric current is passed, have already been noticed (p. 714). R. Sabine (*Phil. Mag.* [5], ii. 481) has studied the same phenomenon with the following results: (1). The electro-motive force between two surfaces of mercury proceeds from the different degrees of oxidation of these surfaces. 2. The contraction or expansion consequent on the passage of a current between a drop of water and a surface of mercury is equal to the change of volume due to the formation of mercurous oxide. 3. The other best known phenomena of impulsion are to be attributed to this cause, and not to alteration of the capillarity-constants, which, contrary to Lippmann's view (*Pogg. Ann.* cxlix. 546), have but little to do with the electromotive force of the surface.

Detection of Mercury.—To detect the presence of mercury in urine, Mayençon a. Bergeret (*J. Pharm. Chim.* [4], xvii. 148) acidulate the liquid with a few drops of sulphuric acid, and suspend within it, for about half an hour, an iron nail attached to a platinum wire; then, after washing and drying the mercury precipitated on the wire, they introduce it into an atmosphere of chlorine, whereby it is converted into mercuric chloride, and demonstrate the presence of this compound by rubbing the wire with a piece of paper moistened with aqueous potassium iodide, whereby a bright red streak is produced.

Estimation.—J. B. Hannay (*Chem. Soc. J.* xxvi. 565) has devised a method of estimating mercury volumetrically, depending on the fact that the precipitate formed by a few drops of ammonia in a solution of mercuric chloride, disappears completely on addition of a solution of potassium cyanide, whereby the mercuric chloride is converted into cyanide. The mercury must be in the form of mercuric chloride, into which, if previously precipitated as sulphide, it is easily converted by the action of nitromuriatic acid. A comparison of this method with the electrolytic estimation as

metallic mercury, showed that the reduction of mercury takes place most completely from the sulphate, less completely from the nitrate, in presence of free nitric acid, and least of all from the chloride, but that complete reduction may be obtained by previously converting the chloride into cyanide by the action of potassium cyanide.

Tuson a. Neison (*ibid.* xxxii. 679) modify this method by adding to the solution (either acid or neutral) a small quantity of ammonium chloride, then potassium carbonate, till a precipitate appears, and lastly the titrated solution of potassium cyanide, till the liquid becomes perfectly clear. By this modification the method is rendered applicable to the nitrate, sulphate, and other salts of mercury, as well as to the chloride.

Another method of estimating mercury volumetrically is described by J. Volhard (*Liebig's Annalen*, etc. 1), based upon the fact that mercuric salts decolorise the red solution of ferric thiocyanate, quickly in all cases, but completely only when they are added in slight excess. A similar effect is produced by silver, and the volumetric method founded upon it will be described in connection with that metal. In the case of mercury the solution must be slightly acid, and the results obtained with it are not quite exact, but sufficiently so for most purposes.

Compounds of Mercury.

Amalgams. Observations on the behaviour of amalgams at temperatures a little above the boiling point of mercury have been made by E. de Souza (*Deut. Chem. Ges. Ber.* viii. 1616). Silver-amalgam heated to the temperature of boiling sulphur till its weight became constant was found to contain 12.61 to 12.74 per cent. mercury, answering to the formula Ag^{13}Hg . Gold-amalgam similarly treated retained 10.02 to 10.5 per cent. Hg, answering to Au^{11}Hg .

By mixing 20 to 30 pts. of copper reduced by hydrogen with sulphuric acid and 79 pts. of mercury, a mass is obtained which, when freed from sulphuric acid by boiling water, forms after 10 to 12 hours a moderately solid amalgam having the lustre and polish of gold and becoming plastic when heated (*Moniteur Scientifique*, [3], vii. 312, 1877).

Chlorides. The resolution of calomel into mercuric chloride and metallic mercury is not complete at 440° . A gilt silver tube immersed in the vapour of calomel at this temperature, and kept cool by a stream of cold water running through it, becomes coated with a grey film of calomel mixed with only a small quantity of metallic mercury (Debray, *Compt. rend.* lxxxiii. 330).

Mercuric Chloride has been found native in a volcanic district on Ternate, one of the Molucca Islands (Frenzel, *Min. Mitth.* 1877, 305).

Mercuric chloride is reduced to mercurous chloride by the action of hypochlorites, the reaction being complete in boiling acid solutions (T. Fairley, *Rep. Br. Assoc.* 1875, [2], 42).

Amidochloride.—The action of the halogen-elements on white precipitate and other chlorine-compounds of metallic amides has been examined by V. Schwarzenbach (*Deut. Chem. Ges. Ber.* viii. 1231). It is well known that when a mixture of white precipitate and iodine (2 grams white precipitate and 5.04 iodine = 5 at. I to 2 mol. precip.) is drenched with alcohol, an explosion takes place after a while (about 35 minutes). If the alcohol be replaced by carbon sulphide, propyl alcohol, amyl alcohol, chloroform, or glycerin, no explosion takes place even after 24 hours; but if the quantity of iodine be increased to the proportion of 6 at. to 2 mol. white precipitate, the addition of chloroform or amyl alcohol produces a sharp detonation within the liquid, without, however, shattering the vessel. The gas evolved in the explosion produced by alcohol is nitrogen. Chlorine gas likewise acts very strongly on white precipitate. When this substance in powder is introduced into an open flask filled with chlorine, it becomes very hot in a few minutes, acquires a wavy motion, and either explodes immediately, or more frequently exhibits a bright glow and a green flame which lasts for some time. Similar effects are produced with bromine. The chlorides, bromides, and iodides of the alcohol-radicles do not act upon white precipitate, at least at ordinary temperatures and in open vessels; ethyl chloride not even at 30° and under increased pressure. Acetyl chloride produces acetamide, together with a red body which is soluble in alcohol, and contains mercury, nitrogen, and chlorine.

The action of iodine on white precipitate in presence of alcohol always produces nitrogen iodide; the addition of a small quantity of phenol prevents this reaction, however, but gives rise to the formation of a not inconsiderable quantity of iodoform. Phenol, iodine, and white precipitate without alcohol, do not produce iodoform.

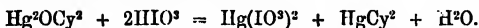
Bromine acts like iodine, giving rise, with alcohol, phenol, and white precipitate, to the formation of bromoform, which may be separated by distillation from the mercuric bromide simultaneously formed (C. Rice, *Pharm. J. Trans.* [3], vi. 765).

Mercurous Iodide, Hg_2I_2 . The crystals of this compound have been examined by Des Cloizeaux (*Compt. rend.* lxxxiv. 1418). It is completely isomorphous with mercurous chloride. The crystals, which are yellow when recently prepared, but turn brown on exposure to the air, are quadratic, exhibiting the faces $\infty\text{P}\infty$, 0P and P , and are usually tabular from predominance of the two parallel prismatic faces, those of P appear also very unequally developed. Axes, $a : b = 1 : 1.6726$. Observed angles, $\text{P} : 0\text{P} = 67.5^\circ$; $\text{P} : \text{P} = 81^\circ 16'$; $\text{P} : \infty\text{P}\infty = 49^\circ 22'$. The crystals usually cleave with moderate facility parallel to 0P , and exhibit strong positive double refraction.

Mercuric Cyanide. Double compounds of this salt with the chlorides of the rarer earth-metals have been prepared by J. E. Ahlén (*Bull. Soc. Chim.* [2], xxvii. 365). These compounds, which are represented by the general formula $\text{RCl}^3.3\text{Hg}(\text{CN})^2 + 8\text{H}_2\text{O}$, are very soluble, and crystallise from solutions containing excess of the chloride; they give off their water of crystallisation over sulphuric acid or at 100° .

Cerium double salt.	$\text{CeCl}^3.3\text{Hg}(\text{CN})^2.8\text{H}_2\text{O}$	Asbestos-like needles.
Lanthanum „	$\text{LaCl}^3.3\text{Hg}(\text{CN})^2.8\text{H}_2\text{O}$	Colourless silky needles.
Didymium „	$\text{DiCl}^3.3\text{Hg}(\text{CN})^2.8\text{H}_2\text{O}$	Reddish flexible needles.
Yttrium „	$\text{YCl}^3.3\text{Hg}(\text{CN})^2.8\text{H}_2\text{O}$	Colourless radiate prisms, giving off only $1\frac{1}{2}\text{H}_2\text{O}$ over sulphuric acid.
Erbium „	$\text{ErCl}^3.3\text{Hg}(\text{CN})^2.8\text{H}_2\text{O}$	Reddish prisms resembling the yttrium salt.

Iodate, $\text{Hg}(\text{IO}_3)^2$. This salt is precipitated in the amorphous state on adding iodic acid to a solution of mercuric oxycyanide:



The same precipitate is obtained from a solution of mercuric nitrate or acetate, but not from the chloride.

Mercuric iodate is a white amorphous powder, insoluble in water, and only slightly attacked by nitric acid, readily however by hydrochloric acid and the chlorides, bromides, iodides, cyanides, and cyanates of the alkali-metals, also by sodium thio-sulphate and by dilute solutions of the chlorides of manganese and zinc. It is insoluble in potash, soda, and ammonia, sodium sulphide, borax, sodium phosphate, alkaline iodates, bromates, and chlorates, and in acetic, hydrofluoric, and silico-fluoric acid. On evaporating a solution of the salt in an alkaline chloride, an iodate of the alkali-metal crystallises out first, then mercuric chloride, and when the solvent is in excess, a series of crystallised double salts is obtained. A solution of mercuric iodate in sodium thio-sulphate yields, on addition of hydrochloric acid, a red precipitate which disappears in excess of the acid. The solution of the iodate in ammonium chloride gives with ammonia a white precipitate insoluble in excess (C. A. Cameron, *Chem. News*, xxxiii. 253).

Oxides. On the Heat of Formation of Mercurous and Mercuric Oxides, see HEAT (p. 955). On the Heat of Combination of Mercuric Oxide with Acids, see pp. 957, 998.

On the Decomposition of Mercuric Oxide by Heat, see p. 1010.

Mercuric Sulphide, HgS . *Preparation of Vermillion.*—This modification of mercuric sulphide may be prepared by the action of sodium thio-sulphate on mercuric ammonium chloride. A solution of mercuric chloride is poured into an excess of dilute aqueous ammonia, and a strong solution of sodium thio-sulphate is stirred into the liquid in quantity rather more than sufficient to dissolve the resulting precipitate. On warming the solution in a basin, the separation of vermillion immediately begins, and the heating must be continued till the whole acquires a pasty consistence. The ammonia and sal-ammoniac contained in the solution appear to exert an essential influence both on the formation and on the appearance of the product; its appearance is likewise affected by the temperature kept up during the evaporation. At 50° – 60° a lighter-coloured preparation is obtained than at 90° – 100° . The finest vermillion is produced at 70° – 80° (O. Hausmann, *Deut. Chem. Ges. Ber.* vii. 1746).

L. Raab (*N. Rep. Pharm.* xxiv. 39) heats sublimed and finely-triturated calomel with a solution of sodium thio-sulphate, decants the resulting black mercury sulphide, and drenches it with a solution of liver of sulphur (prepared from pure potassium

carbonate). The solution is then evaporated, with stirring, to complete dryness, and the residue when cold is washed with warm water till all soluble matters are removed. On again drenching it with solution of liver of sulphur, and evaporating down, the black mercuric sulphide passes into the red modification.

Reactions.—1. Vermillion prepared in the wet way by digesting metallic mercury with ammonium pentasulphide is decomposed by light much more rapidly than sublimed vermillion, the depth and rapidity of the blackening varying according to the nature of the supernatant liquid, the change being especially rapid under alkaline liquids (K. Heumann, *Ber.* vii. 750).

2. Vermillion is rapidly decomposed by boiling with water and finely-divided copper, the products being metallic mercury, copper sulphide, and a dark-coloured powder insoluble in nitric acid, which is turned white by boiling with strong nitric acid, black again by contact with alkalis, and once more white by boiling with nitric acid. The white compound thus produced has the composition $2\text{HgS} \cdot \text{Hg}(\text{NO}_3)_2$, and is identical with the white precipitate formed by passing a small quantity of hydrogen sulphide into a solution of mercuric nitrate; it may also be produced by digesting mercuric sulphide with a strong solution of the nitrate. The blackening of this compound arises from separation of mercuric sulphide. When moistened with caustic soda, it first turns yellow, then brown, and finally black; if heat be applied, however, it turns black almost immediately. The black substance is an oxysulphide, $\text{HgO} \cdot 2\text{HgS}$. Dilute acids dissolve out the oxide, and when the compound is boiled with strong nitric acid, the resulting mercuric nitrate combines with the separated sulphide, reproducing the white compound. The statements of Palm (*Jahresb. f. Chem.* 1862, 223) respecting the formation of red addition-products of cinnabar and mercuric salts are erroneous, nothing but white compounds being thus obtained. The decomposition of mercuric sulphide by copper is the cause of the well-known deterioration of the colour of vermillion by contact with copper and brass: hence the means recommended by Karmarsch for preventing this deterioration, viz., exhausting the vermillion with a solution of pearlsh, or bringing it in contact with water and slips of copper to remove admixed sulphur, are useless.

Zinc powder likewise decomposes mercuric sulphide even more rapidly than copper powder, vermillion prepared in the wet way being likewise in this case decomposed much more rapidly than sublimed vermillion; the products are zinc sulphide, zinc amalgam, and metallic mercury. On adding vermillion to zinc powder previously drenched with hydrochloric acid, hydrogen sulphide is immediately evolved, and the colour is destroyed. This shows that mercuric sulphide is likewise decomposed by nascent hydrogen (Heumann, *Dent. Chem. Ges. Ber.* vii. 752, 1388 and 1486).

Mercuric sulphide is insoluble in caustic soda-ley and in sodium monosulphide, but dissolves in a mixture of the two; with 2 pts. crystallised sodium sulphide, 2 pts. soda-ley of sp. gr. 1.33, and 1 pt. mercuric sulphide, an orange-red solution of mercury-sodium sulphide is obtained which filters readily. On heating this solution with water, black mercuric sulphide separates, and by adding a sufficient excess of water the whole of the mercury may be removed from the liquid; if, however, an excess of alkali is present, the complete precipitation of the mercury cannot be effected. Mineral acids, organic acids, and hydrogen sulphide produce an immediate precipitate of black amorphous sulphide. If the liquid be left to itself in a loosely closed vessel, it absorbs carbonic acid, gives off hydrogen sulphide, and deposits, first, crystals of sodium carbonate mixed with 5 per cent. mercury sulphide, afterwards red and red-brown crystals of mercury sulphide, which are finer and more regular the more slowly the absorption of carbonic acid takes place. These crystals are hexagonal prisms or plates which react chemically like cinnabar (Méhu, *Russ. Zeitschr. Pharm.* 1876, 321).

Compound of Mercuric Sulphide with Cuprous Chloride, $2\text{HgS} \cdot \text{Cu}^2\text{Cl}^2 = \text{Cl} \cdot \text{Cu} \cdot \text{S} \cdot \text{Hg}$ — $\text{Hg}_2\text{S} \cdot \text{Cu} \cdot \text{Cl}$.—When red or black mercuric sulphide is boiled with a solution of cupric chloride, no reaction takes place at first; but, on adding strong hydrochloric acid, a brilliant orange-powder is immediately formed, whilst the liquid assumes a dark brown colour due to the formation of cuprous chloride, which dissolves with that colour in the excess of cupric chloride. The yellow precipitate contains a large quantity of admixed sulphur, which, however, may be easily removed by solution in carbon sulphide. The formation of this compound may be represented by the equation:



The formation of cuprous chloride is probably also partly due to another reaction represented by the equation $\text{HgS} + 2\text{CuCl}^2 = \text{HgCl}^2 + \text{Cu}^2\text{Cl}^2 + \text{S}$, partly to a secondary action of the excess of cupric chloride on the previously formed yellow body. Strong

hydrochloric acid, boiled with the compound $2\text{HgS} \cdot \text{Cu}^2\text{Cl}_2$, dissolves out cuprous chloride and mercuric chloride, with slight evolution of hydrogen sulphide. Dilute sulphuric acid exerts no action on the compound even at the boiling heat; but the boiling concentrated acid decomposes it, with elimination of hydrogen chloride and sulphur dioxide, forming a compound of mercuric sulphate and sulphide. Caustic soda colours the yellow compound deep black, removing all the chlorine, and replacing it by oxygen, whence there results a mixture of 2 mol. HgS and 1 mol. Cu_2O . Dilute hydrochloric acid heated with this mixture dissolves a large quantity of mercury but only a small quantity of copper, the reaction, as shown by direct experiment, taking place according to the equation:



Cuprous or cupric sulphide digested with mercuric chloride yields nothing but the white compound $2\text{HgS} \cdot \text{HgCl}_2$ (Heumann, *Deut. Chem. Ges. Ber.* vii. 1390).

Analysis.—For the quantitative analysis of native cinnabar, Fr. Gramp (*J. pr. Chem.* [2], xi. 77) oxidises it with nitric acid of sp. gr. 1.4 in a sealed tube at 120° , whereby complete solution is effected.

An analysis by C. W. Dabney of native cinnabar from Canyon City, Oregon, has been published by J. W. Mallet (*Chem. News*, xxxiv. 180). This cinnabar is remarkable for giving off hydrogen sulphide when treated with hydrochloric acid, then yielding a small quantity of sulphur when heated in a sealed tube, then again giving off hydrogen sulphide when heated with hydrochloric acid, which, at the same time, dissolves iron. The analysis of the mineral, which forms veins in calcspar, gave:

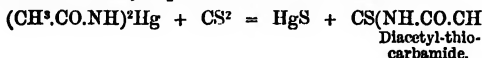
Hg	S ⁽¹⁾	S ⁽²⁾	Fe	SiO ²	O ⁽³⁾
78.42	0.54	13.59	4.09	3.06	0.30 = 100.
(1) Given off as H ² S.		(2) In the residue.		(3) By difference.	

The double reaction is explained on the supposition that the iron is present partly as magnetic pyrites, partly as iron pyrites. Supposing part of the sulphur to be combined with the mercury as HgS , then calculating the quantity given off in the form of H²S as Fe^2S^2 , the remaining sulphur as FeS^2 , and the rest of the iron as Fe^2O^3 , we have:

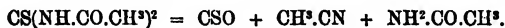
HgS	Fe ² S ²	FeS ²	Fe ² O ³	SiO ²
90.97	1.37	1.95	3.36	3.06 = 100.71.

To the presence of similar mixtures of iron sulphides containing different proportions of sulphur, Mallet likewise attributes the differences in the analyses of cinnabar from other localities (e.g. from Japan, analysed by John), which have given, instead of 32 pts. sulphur, as much as 44.64 pts. to 200 of mercury.

MERCURY-ACETAMIDE, $\text{C}^4\text{H}^5\text{N}^2\text{O}^2\text{Hg}$ = $(\text{CH}^3 \cdot \text{CO} \cdot \text{NH})^2\text{Hg}$. This compound, produced by saturating an aqueous solution of acetamide with mercuric oxide (i. 7), is decomposed by heating to 100° in sealed tubes with carbon disulphide, yielding mercuric sulphide, carbon oxysulphide, acetoneitril, and acetamide:



and



Iodine (not in excess) and thiocarbonyl likewise separate large quantities of acetamide from its mercury-compound. Mercury-acetamide is completely decomposed by hydrogen sulphide in alcoholic solution, behaving, therefore, with various reagents in the same manner as mercury-benzamide. Both these compounds are also decomposed in a similar manner by dry distillation, yielding large quantities of the acid amide, together with water, ammonia, carbon, and metallic mercury; the benzamide-compound also yields benzonitril (Oppenheim a. Pfaff, *Deut. Chem. Ges. Ber.* vii. 623).

Phenyl-mercuracetamide or **Mercuracetanilide**, $(\text{CH}^3 \cdot \text{CO} \cdot \text{N} \cdot \text{C}^6\text{H}^5)^2\text{Hg}$, is formed by fusing acetanilide with mercuric oxide, and crystallises from alcoholic solution in small colourless needles which melt, with partial decomposition, at 215° , and are completely decomposed by hydrogen sulphide.

MERCURY-BENZAMIDE, $(\text{C}^6\text{H}^5 \cdot \text{CO} \cdot \text{NH})^2\text{Hg}$. See BENZAMIDE (p. 155).

MERCURY-DICYMYL, $(\text{C}^{10}\text{H}^{13})^2\text{Hg}$, is formed by heating a mixture of bromocymene and xylene with sodium-amalgam, with addition of a little acetic ether. It forms long slender needles, which melt at 134° , and dissolve with moderate facility in boiling alcohol, very sparingly in cold alcohol, more readily in benzene and in xylene. It volatilises without decomposition.

MERCURY-PHENYLXANTHAMIDE. See XANTHAMIDE.

MERCURY THIOCYANATE. See THIOCYANATES.

MESACONIC ACID, $C^8H^6O^4$. See PYROCITRIC ACIDS, under CITRIC ACID (pp. 511, 518); also PYROTARTARIC ACID.

MESADIBROMOPYROTARTARIC ACID. See PYROTARTARIC ACID.

MESIDINE. See MESITYLENES (AMIDO-); also CUMIDINE (p. 592).

MESITOL, $C^9H^{12}O = C^9H^{11}.OH$ (Biedermann a. Ledoux, *Deut. Chem. Ges. Ber.* viii. 57). Mesidine nitrate, treated with nitrous acid, yields a solution of diazo-mesitylene nitrate, and on distilling this solution, a large quantity of gas is given off, and mesitol passes over with the aqueous vapour, solidifying partly in the condensing tube, partly in the receiver. Mesitol is also formed, together with another body, most probably oxymesitylenic acid, by fusing potassium mesitylenesulphonate with potassium hydroxide. On acidulating the melt with sulphuric acid, and distilling with water, the mesitol passes over with the steam at the beginning of the distillation.

Mesitol has a strong odour of phenol, dissolves very easily in alcohol, ether, and benzene, floats on water, volatilises very readily with aqueous vapour, and crystallises at the same time in very beautiful long white needles. It melts at 68° – 69° , and boils at 215° – 220° .* Mesitol dissolves very easily in the fixed alkalis, and is precipitated therefrom in the crystalline state by hydrochloric acid. It does not dissolve in ammonia or in alkaline carbonates. No nitro-derivatives of it have been obtained. Treated in acetic acid solution with bromine, it forms monobromomesitol, which is precipitated by water in white flocks, and crystallises from alcohol in slender needles having a silky lustre and melting at 80° .

MESITYL OXIDE, $C^9H^{10}O$. This compound is formed, together with other products, by the action of zinc-methyl or zinc-ethyl on acetone (Pawlow, *Deut. Chem. Ges. Ber.* ix. 1311); also in small quantity, together with ammonia and other bases, by the distillation of diacetonamine (Heintz, *Liebig's Annalen*, clxxiv. 133; clxxxi. 70; *Ber.* viii. 768).

Mesityl oxide, as well as phorone, is converted by strong sulphuric acid, for the most part, into mesitylene (Claisen, *Ber.* vii. 1168). By prolonged boiling with dilute nitric acid, resinous products are formed at first, afterwards acetic and oxalic acids. Bromine acts violently on mesityl oxide, with evolution of hydrogen bromide; but a solution of mesityl oxide in carbon sulphide takes up bromine directly, forming the compound $C^9H^{10}O.Br_2$. As the solvent evaporates, this dibromide remains in the form of a dark-coloured oil which becomes yellowish on distillation with steam. It is, however, only comparatively permanent under water; in the dry state it assumes, after a few hours, a deep violet colour, and slowly gives off hydrogen bromide. It cannot be distilled even in a vacuum. An alcoholic solution of mesityl oxide is strongly attacked by sodium-amalgam; and if, after the odour of the mesityl oxide is no longer perceptible, the solution be precipitated with water, and the oil thereby thrown down be subjected, after drying, to distillation, the greater part ($\frac{3}{4}$ of it) passes over between 205° and 225° , and of this the principal fraction at 213° – 217° . This fraction has the composition $C^{12}H^{20}O$. Sometimes, also, there is formed a small quantity of a solid body which melts between 110° and 120° (Claisen, *Ber.* viii. 1256).

MESITYLENE, $C^9H^8(CH^3)^3$ [1 : 3 : 5], and **PSEUDOCUMENE**, $C^9H^8(CH^3)^3$ [1 : 2 : 4] (Jacobsen, *Liebig's Annalen*, clxxxiv. 179; *Ber.* ix. 256; x. 855). These two modifications of trimethylbenzene occur together in coal-tar oil, and cannot be effectually separated by the usual methods of fractional distillation, or fractional crystallisation of the barium salts of their sulphonic acids. The separation may, however, be effected by converting them into the amides of their sulphonic acids. For this purpose, the portions of commercial cumene from coal-tar oil, boiling between 160° and 168° , and freed from phenol, are agitated with ordinary sulphuric acid, and the resulting sulphonic acids are converted into barium salts and then into sodium salts; the latter in the state of dry powder are triturated with an equal weight of phosphorus pentachloride; the product is freed from phosphorus oxychloride by heating; and the residual semifluid mass, when cold, is added to a large excess of concentrated aqueous ammonia. The resulting sulphamides, which harden after a few days to a crystalline mass, are washed with water, dissolved in alcohol, and separated from one another by distilling off the alcohol and leaving the residue to crystallise, whereupon the pseudocumenesulphamide crystallises out first, and then the mesitylenesulphamide.

To obtain the hydrocarbons from these sulphamides, the latter are heated in

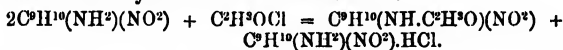
* Fittig a. Hoogewerff (*Liebig's Annalen*, cl. 323), by heating potassium mesitylenesulphonate with potash, obtained a phenol to which they assigned the formula $C^9H^{10}O$ (*xylenol*, vi. 1128). It is described as melting at 70° – 73° , boiling at 216° – 217° , and yielding with bromine a dibromo-derivative which Biedermann a. Ledoux were not able to obtain.

sealed tubes with strong hydrochloric acid, the mesitylenesulphamide to about 160°, the pseudocumenesulphamide to about 170°. The hydrochloric acid must be used in considerable excess, as otherwise the products will consist of the corresponding dimesitylene- and dipseudocumene-sulphamides, especially if the temperature required for the decomposition be not continued long enough.

The mother-liquors of mesitylene and pseudocumene thus obtained, yielded, when treated as above described, sulphamides melting respectively at 130° and 100°–102°; and both of these sulphamides, when heated with hydrochloric acid, yielded one and the same hydrocarbon, boiling at 138°–140°, which is the boiling point of metaxylene. Crude coal-tar cumene contains, therefore, only two trimethylbenzenes, viz. mesitylene and pseudocumene; and the great difficulty of separating these two hydrocarbons arises from the fact that they obstinately retain, not, as might be expected, a third trimethylbenzene, but a dimethylbenzene, viz. metaxylene. That the separation of the two trimethylbenzenes cannot be effected through the medium of the barium salts of their sulphonic acids is due to the formation of a molecular compound of these two barium salts, which may, in fact, be directly obtained by crystallising the two together (p. 1285).

Mesitylene is also formed: α . By the action of strong sulphuric acid on mesityl oxide and on phorone (from acetone) (Claissen, *Ber.* vii. 1168). β . By polymerisation of allylene, $\text{CH}_2=\text{C}=\text{CH}$ (prepared by the action of alcoholic potash on propylene bromide, and purified by conversion into the copper compound) under the influence of strong sulphuric acid. The allylene is absorbed by the acid in large quantity, forming a brown-yellow solution, which when diluted with a little water and distilled, yields a distillate consisting of two layers, the upper of which is nearly pure mesitylene. The polymerisation of the allylene takes place, not during its absorption by the sulphuric acid, but in the subsequent distillation (Fittig a. Schroe, *Ber.* viii. 17; Jacobsen, *ibid.* x. 855).

Nitro- and Amido-mesitylenes (Ladenburg, *Ber.* vii. 1133; *Liebig's Annalen*, clxxix. 163).—Dinitromesitylene is converted by ammonium sulphide into the nitromesitylene, $\text{C}_6\text{H}(\text{CH}_3)_2(\text{NO}_2)(\text{NH}_2)$, discovered by Maule (iii. 930), which melts at 72°–73°, and crystallises in large thick yellow prisms when left to cool slowly from the state of fusion. By the action of acetyl chloride it is converted into nitroacetyl-mesitylene and hydrochloride of nitromesitylene:



The quantity of nitroacetyl-mesitylene is however greater, and that of nitromesitylene hydrochloride less than that which corresponds with the preceding equation; the nitromesitylene hydrochloride may be dissolved out of the crude product by warm water.

Nitroacetyl-mesitylene forms nearly colourless needles having a silky lustre; it melts at 188°, and distils without decomposition; dissolves easily in warm alcohol even when dilute. By fuming nitric acid, or better by a mixture of nitric and sulphuric acids, it is converted into dinitroacetyl-mesitylene, $\text{C}_6\text{H}^8(\text{NHC}_2\text{H}_3\text{O})(\text{NO}_2)_2$, which crystallises from hot alcohol, in which it is but slightly soluble, in shining white needles melting at 275°. The dinitromesitylene, $\text{C}_6\text{H}^8(\text{NH}_2)(\text{NO}_2)_2$, obtained by heating this acetyl-compound to 160° with hydrochloric acid, melts at 193°–195°, and is identical with that which Fittig obtained (vi. 300) by reduction of trinitromesitylene. On drenching it with alcohol saturated with nitrous acid, it becomes very hot, so that it is necessary to add the alcohol only gradually and to moderate the action by cooling. The resulting dinitromesitylene, $\text{C}_6\text{H}^8(\text{NO}_2)_2$, forms nearly colourless shining needles, melts at 86°, and is identical with the dinitromesitylene discovered by Hofmann (iii. 930).

Mononitromesitylene, $\text{C}_6\text{H}^{11}(\text{NO}_2) = \text{C}_6\text{H}^2(\text{NO}_2)(\text{CH}_3)^3$.—The mode of preparing this compound given by Fittig and Storer (vi. 299) yields it in small quantity only. Larger quantities are obtained by distilling with steam the oil which remains when the last mother-liquors of the preparation of dinitromesitylene are left to evaporate. The same nitromesitylene is obtained by converting dinitromesitylene into nitromesitylene, and treating the latter with nitrous acid and alcohol. It melts at 42°, and boils at 255°. By tin and hydrochloric acid it is reduced to amidomesitylene, $\text{C}_6\text{H}^{11}(\text{NH}_2)$, boiling at 229°–230°, and remaining liquid at –15°. The *platinocliloride* of this base, $(\text{C}_6\text{H}^{11}\text{NH}_2.\text{HCl})_2\text{PtCl}_4$, is nearly insoluble in hot water, and crystallises from strong hydrochloric acid in needles having a golden-yellow shimmer.

Acetylamidomesitylene, $\text{C}_6\text{H}^{11}(\text{NH}_2\text{C}_2\text{H}_3\text{O})$, prepared from the preceding base by the action of acetyl chloride, or by heating with glacial acetic acid, melts at 216°–217°, and sublimes in needles without decomposition. It dissolves in nitric acid of sp. gr. 1.4, and is precipitated therefrom by water without alteration. If, however, it be

added to fuming nitric not too highly concentrated, and the liquid be gradually mixed with water, nitro-acetyl-mesitydine gradually separates. The nitro-base thus produced crystallises from alcohol in white needles melting at 186° – 188° , and is identical with the nitro-acetyl-mesitydine obtained, as above mentioned, by acetylation of nitro-mesitydine. Like the latter it yields, when heated to 160° with hydrochloric acid, the nitromesitydine which melts at 71° .

Mesitylene-acediamine, $C^9H^{10}(NH.C^2H^3O)^2$, is obtained by boiling mesitylene diamine, $C^9H^{10}(NH^2)^2$, with glacial acetic acid. It melts at a temperature above 300° , and is nearly insoluble in water and in dilute hydrochloric acid (Ladenburg, *Ber.* viii. 677).

Mesitylenesulphonic acid, $C^9H^{11}(SO^2H) = C^9H^2(CH^3)^3(SO^2.OH)$, crystallises in prisms containing 2 mols. H^2O . *Barium Mesitylenesulphonate*, $(C^9H^{11}SO^2)^2Ba + 9H^2O$, is obtained, by slow evaporation of its solution, in large monoclinic tables; by more rapid crystallisation in long flat prisms acuminate on both sides, 5.53 parts of which dissolve in 100 pts. water at 11.5° . At the same temperature 4.19 pts. of the anhydrous salt dissolve in 100 pts. of water (Jacobsen).

Mesitylenesulphamide, $C^9H^{11}SO^2NH^2 = C^9H^2(CH^3)^3(SO^2NH^2)$, crystallises from alcohol as a white, long-fibred, asbestos-like mass, from hot water in capillary needles. 1 part of it dissolves in 185 pts. boiling water, and in about 3000 pts. water at 0° , in 0.88 pt. boiling alcohol of 83 per cent., and in 18 pts. of the same alcohol at 0° . In ether it is less soluble than in alcohol; it dissolves also in strong sulphuric acid and in alkalis. Melting point 141° – 142° (Jacobsen). By oxidation with potassium dichromate and sulphuric acid it is converted into parasulphamine-mesitylenic acid, $C^9H^2(CH^3)^3(SO^2NH^2)(CO^2H)$. See MESITYLENIC ACID (p. 1285).

Dimesitylenesulphamide, $(C^9H^{11}SO^2)^2NH$, formed by heating the preceding compound with hydrochloric acid not in excess, and not long enough to effect its complete decomposition (p. 1283), is moderately soluble in hot water, and crystallises therefrom in needles which melt at 124° , and are partly decomposed on volatilisation (Jacobsen).

Pseudocumene or **Unsymmetrical** **Trimethylbenzene,**

$C^6.CH^3.CH^3.H.CH^3.H.H$, is obtained: 1. From coal-tar cumene in the manner already described (p. 1282), or more simply by agitating the crude coal-tar cumene with strong sulphuric acid, mixing the acid mass with about five times its bulk of water, syphoning off the layer of dilute sulphuric acid which sinks to the bottom, diluting the remaining liquid with four times its bulk of water, and leaving the clear warmed solution to crystallise, whereupon it deposits cubes of pseudocumenesulphonic acid. These, when purified by crystallisation and heated, yield a distillate of pure pseudocumene (Jacobsen, *Ber.* ix. 258). 2. By dehydration of phorone with phosphoric anhydride,* $C^9H^{14}O - H^2O = C^9H^{12}$. 100 pts. phorone (from acetone) are heated in a sand-bath with 75 pts. phosphoric anhydride mixed with twice its weight of sand, the mixture being slowly distilled to dryness and the distillate fractionated. The greater part of it is found to consist of pseudocumene, identical in its properties with that obtained from coal-tar oil (Jacobsen, *Ber.* x. 855). 3. By the action of methyl iodide and sodium at 100° in a reflux apparatus on the dibromotoluene, $C^6.CH^3.Br.H.Br.H^2$, prepared by exposing a mixture of ortho- and para-bromotoluene to the action of bromine and iodine in sunshine (Fittig & Jannasch, *Liebig's Annalen*, cli. 283; Jannasch, *ibid.* clxxvi. 283). 4. As a bye product, in the preparation of dur-one (tetramethylbenzene) from dibromoxylene, methyl iodide, and sodium (Jannasch, *loc. cit.*)

Pseudocumene boils at 166° , and is oxidised by dilute nitric acid to paraxylic acid, $C^6H^3(CH^3)^3(CO^2H)$, and xylydic acid, $C^6H^3(CH^3)(CO^2H)^2$ (vi. 1129).

Pseudocumenesulphonic acid, $C^6.CH^3.CH^3.H.CH^3.H.SO^2H$.—The barium salt of this acid separates from solution at ordinary temperatures in anhydrous crystalline scales; but on leaving its solution to evaporate over sulphuric acid, at a temperature between 0° and 5° , the salt separates in limpid rhombic tables or rhombohedral crystals which contain 2 mol. water and effloresce very easily.

When the barium salts of pseudocumenesulphonic and mesitylenesulphonic acids, previously deprived of their water of crystallisation, are crystallised together in molecular proportions, there is obtained, whether the crystallisation takes place at the ordinary or at a lower temperature, an anhydrous double salt composed of pseudocumenesulphonate and mesitylenesulphonate of barium; this result confirms what has already been said (p. 1283) about the difficulty of separating the two hydrocarbons by means of their barium sulphonates. 100 pts. water at 11.5° dissolve 5.81 pts. of this double salt.

* Phorone dehydrated by sulphuric acid yields, as already observed, mesitylene instead of pseudocumene (p. 1283).

Pseudocumenesulphamide, $C^8H^{11}SO^2NH^2$, crystallises from alcohol in short hard prisms, from hot water in laminae, and melts between 175° and 176° . One part of it dissolves in 380 pts. of boiling water, in about 7000 pts. of water at 0° , and in 4.4 pts. of 83 per cent. alcohol at 0° . It is less soluble in other than in alcohol, and behaves to strong sulphuric acid and alkalis like mesitylenesulphamide.

MESITYLENE, HOMOLOGUES OF (Jacobsen, *Ber.* vii. 1430). These bodies are derivatives of benzene containing three alcohol-radicles, C^2H^{2n+1} , in the symmetrical positions 1, 3, 5. The formation of a hydrocarbon having the composition $C^{10}H^{14}$ in the preparation of mesitylene was observed some years ago by Fittig a. Brückner (*Lieb. Ann.* cxlvii. 42), and by Jacobsen (*ibid.* cxlvi. 85), and the formation of a sulphonic acid yielding a sparingly soluble barium salt (like that of the sulphonic acid from the hydrocarbon $C^{10}H^{14}$ just mentioned) was noticed by H. Rose (*ibid.* cxiv. 53). It appeared probable that the source of this hydrocarbon was to be found in the methyl-ethyl ketone which Fittig had detected in crude acetone; and in fact Jacobsen found that pure acetone did not yield any homologues of mesitylene, but that when mixtures of pure acetone (b. p. 58° – 59.5°) with methyl-ethyl ketone were subjected to the process usually adopted for the preparation of mesitylene, large quantities of higher hydrocarbons (b. p. 170° – 230°) were obtained, from which, by fractionation and further methods of purification, three hydrocarbons were isolated, represented by the formulæ $C^{10}H^{14}$, $C^{11}H^{16}$, and $C^{12}H^{18}$.

Dimethylethylbenzene, $C^{10}H^{14} = C^6H^3(CH^3)^2(C^2H^5)$, boils at 180° – 182° , and yields on oxidation mesitylenic acid and a little uvitic acid. Its sulphonic acid crystallises in large needles, and yields a barium salt which crystallises in pearly scales. As it is but sparingly soluble in water, it is easily separated from barium mesitylene-sulphonate, and therefore well adapted for the preparation of the pure hydrocarbon. *Tribromodimethylethylbenzene* is sparingly soluble in alcohol, and crystallises from a hot solution in thin long needles melting at 218° ; it readily sublimes, and distils above 360° . *Trinitrodimethylethylbenzene* crystallises from hot alcohol in hard, long needles melting at 238° .

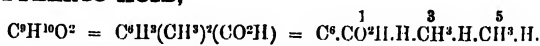
Methyldiethylbenzene, $C^{11}H^{16} = C^6H^3(CH^3)(C^2H^5)^2$, boils at 198° – 200° . On oxidation it yields chiefly uvitic acid, and its tribromo-compound crystallises from hot alcohol in needles melting at 206° .

Triethylbenzene, $C^{12}H^{18} = C^6H^3(C^2H^5)^3$, is obtained in small quantity only by the process above mentioned, much more abundantly (as also methyldiethylbenzene) from those fractions of crude acetone which pass over above 65° ; in very small quantity, on the other hand, by treating nearly pure methyl-ethyl ketone with sulphuric acid. It boils at 217° – 220° , and is oxidised by chromic acid to trimesic acid.

Methyl-dipropyl-benzene, $C^{13}H^{20} = C^6H^3(CH^3)(C^3H^7)^2$, is obtained, together with *Dimethyl-propyl-benzene*, $C^{11}H^{16} = C^6H^3(CH^3)^2(C^3H^7)$, and mesitylene, by carefully distilling 2 vols. methyl-propyl ketone (b. p. 104° – 110°), and 4 vols. acetone with 3 vols. sulphuric acid, and subjecting the portions of the product which boil between 190° and 260° to repeated fractional distillation over sodium. Dimethyl-propyl-benzene boils at 206° – 210° ; methyl-dipropyl-benzene at 243° – 248° . The former when boiled with dilute nitric acid (sp. gr. 1.1) yielded mesitylenic acid, with scarcely any secondary products; the latter gave nothing but uvitic acid, together with a very small quantity of an acid which volatilised with vapour of water.

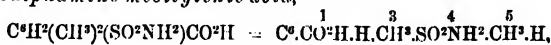
The products of still higher boiling point did not yield any tripropyl-benzene; neither were higher homologues of mesitylene obtained by the action of sulphuric acid on methyl-propyl ketone, or methyl-isobutyl ketone, or methyl-ænantinol (Jacobsen, *Ber.* viii. 1258).

MESITYLENIC ACID,



This acid is formed, together with a very small quantity of uvitic acid, $C^8H^8O^4$, by boiling symmetrical dimethylethylbenzene (p. 1285) with nitric acid of sp. gr. 1.1 (Jacobsen, *Ber.* vii. 1430; Wroblewski, *ibid.* ix. 495).

Parasulphaminic-mesitylenic acid,



is produced by boiling mesitylene-sulphamide for five hours with potassium dichromate (7 pts.) and sulphuric acid (10 pts. diluted with 3 vols. water). It crystallises from its aqueous solution in flat irregular prisms; melts at 217° ; dissolves easily in alcohol and ether, sparingly in boiling water, and is nearly insoluble in cold water. The barium salt is very soluble and difficult to crystallise. The copper salt,

$[C^6H^4(CH^3)(SO^2NH^2CO^2)]^2Cu + 4H^2O$, is precipitated from the solution of the barium salt by cupric sulphate in small blue needles, which, after drying in the air, give off water over sulphuric acid, and recover it on subsequent exposure to the air; at 200° the salt becomes light-green, loses all its water, and is afterwards not altered by contact with the air.

By heating with concentrated hydrochloric acid, parasulphamine-mesitylenic acid is partly converted into mesitylenic acid, which may be separated from the unaltered acid by sublimation (Hall a. Remsen, *Ber.* x. 1039).

MESOCAMPHORIC ACID, $C^{10}H^{16}O^4$. Jungfleisch (*Ber.* vi. 268), by heating dextrocamphoric acid with a little water to 170° – 180° , has obtained an inactive camphoric acid which he has not been able to separate into dextro- and lævo-acid. It crystallises in tufts of needles, and appears to be identical with mesocamphoric acid (vii. 235). Another modification, likewise inactive, and apparently identical with Chautard's paracamphoric acid (vi. 389), is formed by heating camphoric acid to 280° . F. Wreden (*Ber.* vi. 565) remarks that mesocamphoric acid, which he also regards as identical with Jungfleisch's acid, is, according to his own experiments, very easily converted into another inactive modification, probably identical with the second acid obtained by Jungfleisch.

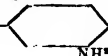
METACINNAMENE or **METASTYROLENE**. C^9H^8 , is formed, together with cinnamene and other products, by heating phenylbromethyl with an alcoholic solution of potassium cyanide (Radziszewski, *Ber.* vii. 140).

METACROLEIN, nC^3H^4O . This polymeride of acrolein, which Gauthier a. Cartmell obtained by heating acrolein hydrochloride with potassium hydrate, is likewise formed, together with ethoxyl-acrolein, $C^3H^5O^2 = C^3H^3(OC^2H^5)O$, and other products, by heating the same salt with sodium ethylate (Taubert, p. 42 of this volume).

METACYANANILINE, $C^{14}H^{14}N^2 =$
$$\begin{array}{c} C(NH) \cdots NH(C^6H^5) \\ | \\ C(NH) \cdots NH(C^6H^5) \end{array}$$

$[NH : CNH = 1 : 3]$. This modification of cyananiline, which melts at 54° , is obtained by distilling uramido-benzoic acid with a fourth of its weight of phosphoric anhydride. Para-uramidobenzoic acid, similarly treated, yields paracyananiline melting at 86° (Griess, *Ber.* viii. 1114).

META-DERIVATIVES, AROMATIC (1 : 3). This article includes a number of meta-derivatives which have not been noticed under the respective primary compounds, and references to a few others, which otherwise might not easily be found.

Metamidobenzoyl-carbamide, $C^6H^5N^3O^2 = H^2N.CO.NH.CO-$  NH^2

See CARBAMIDES (p. 394).

Metabromaniline, $C^6NH^2.H.Br.H^3$. See BENZENES (BROMAMIDO-), p. 193.

Metabromobenzyl Bromide, $C^6H^4Br.CH^2Br = C^6.CH^2Br.H.Br.H^3$. See BENZYL, HALOID ETHERS OF (p. 314).

Metachlor-orthonitraniline, $C^6NH^2.NO^2.H.H.Cl.H$. See BENZENES (CHLORONITRAMIDO-), p. 202.

Metachlor-ortho-oxybenzoic or *Metachlorosalicylic acid*, $C^6.CO^2H.OH.H.H.Cl.H$ (m. p. 172.5°). See BENZOIC ACIDS (Oxy-), pp. 280, 300.

Meta-cresol, $C^6.OH.H.CH^3.H^3$. See PHENOLS.

Meta-cyaniline. See PHENYLAMINES.

Metadibromobenzidine, $C^{12}H^{10}N^2Br^2$. See METAZOXYDIBROMOBENZENE (p. 1287).

Metadicyanobenzene, $C^6H^4(CN)^2$, obtained by distilling the potassium salt of benzene-metadisulphonic acid (p. 251) with potassium cyanide, crystallises in filiform needles, very soluble in water and melting at 156° (Körner a. Monselise, *Gazz. chim. ital.* 1876, 133); according to Limpricht (*Liebig's Annalen*, clxxx. 88) it forms nodular groups of needles melting at 150° .

Meta-hydrazodibromobenzene. See METAZOXYDIBROMOBENZENE (p. 1287).

Metanitrobenzoyl-carbamide, $C^6NH^2.H[CO.NH.CO.NH^2].H^3$ (see the corresponding Amido-compound, *supra*).

Metanitrobenzyl Bromide, $C^6H^4(NO^2).CH^2Br = C^6.CH^2(NO^2).H.Br.H^3$. See TOLUENES (NITRO-).

Metanitro-orthochloraniline, $C^6.NH^2.H.NO^2.H.H.Cl$. See BENZENES (CHLORONITRAMIDO-), p. 203.

Meta-oxyphenyl-urethane, $C^6H^5O.CO.NH(C^6H^5)OH$. See URETHANES.

Meta-oxuyvitic acid. See OXYUVITIC ACID.

Metaphenylene-diamine, $C^6H^2.NH^2.H.NH^2.H^2$. See BENZENES (DIAMIDO), (p. 210).

Metazocarbonylbenzene-Metadimethylamidocarbonylbenzene, or *Carboxylphenylmetazodimethylamidobenzoic acid*,



is formed by the action of metadiazobenzoic acid on metadimethylamidobenzoic acid. It is a reddish-brown precipitate, gradually becoming crystalline, and possessing great tinctorial power (Griess, *Ber.* 1877, 525).

Metazoxydibromobenzene, $C^{12}H^8Br^2N^2O$, is prepared by heating 13 pts. metabromonitrobenzene (m. p. 63°), with 50 pts. alcohol (of about 90 per cent.) and 8 pts. potassium hydroxide; boiling the product for half an hour after the reaction has ceased, then distilling off the alcohol, washing the residual brown-red crystalline mass with water or alcohol, to remove a red colouring matter, and recrystallising it from hot alcohol with addition of animal charcoal, or better from boiling crystallisable acetic acid containing nitric acid. It forms broad, light-yellow prisms, melting at $111^\circ-112^\circ$, soluble in ether, glacial acetic acid, carbon sulphide, benzene, and nitrobenzene; volatilises completely when heated; and forms with strong sulphuric acid a deep yellow solution, turning blood-red when warmed (S. Gabriel, *Ber.* ix. 1405).

Metahydrazodibromobenzene, $C^{12}H^{10}Br^2N^2$, obtained by boiling the preceding compound with ammonium sulphide, forms white or faintly reddish thick prisms, melting at $107^\circ-109^\circ$, easily soluble in ether, benzene, warm alcohol, carbon sulphide, and nitrobenzene. It volatilises without decomposition, and dissolves with yellow colour in strong sulphuric acid. The hydrazodibromobenzene which melts at 130° is a para-compound.

When metahydrazodibromobenzene is boiled with strong hydrochloric acid till complete solution takes place on addition of water, and the solution, after decolorisation with animal charcoal, is supersaturated with ammonia, *metadibromobenzidine*, $C^{12}H^{10}N^2Br^2$, is obtained in white crystals of rhombic habit, melting at 151.5° to 152° , easily soluble in hot alcohol, also in ether, benzene, and nitrobenzene, sparingly in carbon sulphide. The crystals volatilise when heated, turning slightly brown. The *hydrochloride*, $C^{12}H^{10}N^2Br^2.2HCl$, forms white crystalline scales. The *platinchloride* has the formula $2(C^{12}H^{10}N^2Br^2.HCl).PtCl^4$.

Azodibromobenzene, $C^{12}H^8Br^2N^2$, prepared from metahydrazodibromobenzene by oxidation with ferric chloride, or by boiling the alcoholic solution of the same compound with animal charcoal, crystallises in slender needles with oblique end-faces; melts at 125.5° ; volatilises without decomposition; dissolves easily in carbon sulphide, ether, and nitrobenzene, sparingly in alcohol.

Metazoxydiiodobenzene, $C^{12}H^8I^2ON^2$, prepared by heating 10 pts. iodonitrobenzene (m. p. 56°) with 50 pts. alcohol and 8 pts. potassium hydroxide, forms flat yellow needles, which volatilise completely when heated; they are sparingly soluble in cold, easily in hot alcohol, easily also in the other ordinary solvents. Heated to 100° in a sealed tube with alcoholic ammonium sulphide, this compound is converted into *metahydrazodiiodobenzene*, $C^{12}H^{10}I^2N^2$, which melts at $89^\circ-90^\circ$, dissolves readily in the ordinary solvents, and is decomposed by hydrochloric acid, with separation of iodine. *Metazodiiodobenzene*, $C^{12}H^8I^2N^2$, prepared from the last by oxidation with ferric chloride, crystallises in orange-red needles with oblique end-faces; melts at 150° ; dissolves slightly in alcohol, easily in the other ordinary solvents; volatilises when heated (Gabriel, *loc. cit.*)

METADIABASE, METADOLERITE, and METAMELAPHYRE. See MELAPHYRE (p. 1272).

METALS. *Formation in Veins.*—Experiments by St. Meunier (*Compt. rend.* lxxxiv. 638) on the reduction of the noble metals by metallic sulphides, tend to show that the presence of gold in iron pyrites, and more especially that of silver in galena, may be due to reactions of this kind. When sea-water acts on a vein of galena, the small amount of silver which the water contains may become concentrated in the galena. The separation of sulphur which accompanies this reaction may lead to the formation of silver sulphide or to the persulphuration of the lead sulphide. On the supposition that the same reaction may be exerted by sodium sulphide, Meunier suggests that sulphuretted mineral springs may play a certain part in the formation of mineral veins.

On the Electrodeposition of Metals on other Metals, see *Dingl. pol. J.* cccviii.

340, 466; *Jahresb. f. Chem.* 1873, 1007.—*Chem. Centr.* 1874, 1680; *Dingl. pol. J.* cxxi. 74; cxxii. 160, 440; cxxiii. 170, 358; *Jahresb.* 1874, 1092–1095). On the Coating of Iron with Copper, see p. 1118 of this volume.

Casting of Metals under reduced Pressure.—To obviate the defects arising from the enclosure of air-bubbles between the metal and the surface of the mould, Cumin a. Martel (*Engineering*, Dec. 20, 1872; *Dingl. cxxii.* 259) exhaust this enclosed gas at the moment of casting by means of an air-pump. The sides of the mould must, of course, be porous enough to give passage to the air. Such moulds may be formed of gypsum, mixtures of gypsum with graphite or alum, or of graphite alone.

Action of Water containing Soap, Albumin, Glycerin, or other Organic Substances, on Red-hot Metals.—Metals at a red heat are not suddenly cooled by immersion in water containing such substances. When, for example, a red-hot copper ball is plunged into soap-water, the rapid production of steam which would ensue on dipping the ball into pure water does not take place. The ball, in fact, continues to glow in the soap-solution, and is surrounded by a layer of vapour, the surface of which completely reflects the light which falls upon it, so that the copper looks as if it were coated with oxidised silver. On continued immersion, the envelope of vapour gradually diminishes, till finally the soapy water comes in contact with the metal, producing an extremely violent burst of vapour (Barett, *Monit. scient.* [3], iv. 91).

Colouring of Metals.—This may be effected by means of a solution of 42·5 grams sodium thiosulphate in 450 grams water mixed with a solution of 45·5 lead acetate in 225 water. Such a solution, when heated, yields lead sulphide, which, when deposited on metals in a thin film, gives them a fine colour. Iron is thereby coloured steel-blue; zinc brown; brass and bronze gold-yellow; copper red, crimson, chestnut brown, light-blue, or reddish-white, according to the temperature of the bath and the time of immersion. If the lead acetate be replaced by an equal quantity of sulphuric acid, bronze acquires first a red, then a green, and finally a splendid green-red colour (*Iron*, Oct. 1874, 419; *Dingl. pol. J.* cxxv. 93). A black colour may be produced on copper-alloys and on silver by means of deliquescent platinic chloride rubbed on the surface (Weiskopf; *Dingl. pol. J.* cxxv. 470).

METANETHOL-CAMPHOR, $C^{10}H^{12}O$ (Perrencud, *Liebig's Annalen*, clxxvii. 63). This substance, discovered by Gerhardt, is most advantageously prepared as follows: An intimate mixture of anethol (210 pts.) and zinc chloride (750 pts.), is heated in a copper retort, and after a few minutes, when white fumes make their appearance in the receiver, a current of super-heated steam is passed over the mixture, the operation being continued till about 2 litres of water have been evaporated. The metanethol-camphor then condenses, together with the aqueous vapours, in the form of a dark-coloured crystalline mass, which must be freed from water, washed with alcohol containing ether, and recrystallised from hot glacial acetic acid or ether. The product amounts to between 5·5 and 10 per cent. of the anethol employed.

Pure metanethol-camphor forms thin silky needles, felted like asbestos or grouped in large tufts, and exhibiting a fine play of colours in polarised light. It melts at 132° , boils with partial decomposition at a temperature above 300° , but sublimes between 115° and 120° . It does not volatilise with vapour of water at 100° . It dissolves very easily in glacial acetic acid at the boiling heat, less easily in hot ether or alcohol, readily in chloroform, carbon sulphide, benzene, and strong sulphuric acid, sparingly in cold ether, still more sparingly in cold alcohol, and is insoluble in water and in soda-ley.

Metanetholcamphor-sulphonic acid, $C^{10}H^{11}O.SO^2H$, is formed when a solution of the camphor in 4 to 6 pts. of cold strong sulphuric acid is left to itself for some hours. Its **calcium salt**, prepared from the dilute solution of the acid, and purified by recrystallisation from alcohol, forms large fatty-lustrous rectangular plates, often with rounded edges. They contain water of crystallisation, which they give off with efflorescence on exposure to the air. The salt has the composition $(C^{10}H^{11}SO^2)^2Ca + H^2O$ at 120° – 130° , and decomposes at a higher temperature; it dissolves easily in water and in aqueous alcohol, less easily in absolute alcohol. The **barium salt**, $(C^{10}H^{11}OSO^2)^2Ba + H^2O$ (at 126°),* crystallises in concentric groups of thick prisms 1 mm. long, having a strong lustre, and permanent in the air. It dissolves very sparingly in absolute alcohol, somewhat more freely in ordinary alcohol, easily in water. The **sodium salt** forms needle-shaped crystals. The **sulphochloride**, $C^{10}H^{11}O.SO^2Cl$, prepared from the sodium salt by the action of phosphorus pentachloride, crystallises in thick prisms, soluble in ether, glacial acetic acid, and chloroform, and melting at 182° – 183° .

* Deduced from the barium determination (mean 22·94 per cent.), which, however, agrees better with the formula of the anhydrous salt (calc. 23·18) than with that above given (calc. 22·49). The water was not determined directly.

METEORITES. The following article contains descriptions and analyses of a number of meteorites which have been recently examined, and in many cases have been actually seen to fall.

The Meteoric Irons of the Mexican Desert. Daubréelite. J. Lawrence Smith (*Sill. Am. J.* 1876, [3], xii. 107; 1878, [3], xvi. 270) draws attention to the newly discovered masses of meteoric iron occurring in the region of Mexico called the *Bolson de Mapini*, or the Mexican Desert, situated in Cohahuila and Chihuahua, two of the northern provinces of the Mexican Republic. In 1854, three masses were described, two of which were conveyed to the United States; in 1868, eight other masses were conveyed to the States; and in 1871 a still larger block was discovered, estimated to weigh 3500 kilog., near El Para. There is, moreover, some account of a mass yet vaster, to be seen in the very centre of this desolate region.

It was in one of these irons that Smith found the mineral to which he has given the name of *daubréelite*. It consists of shiny black particles, more or less scaly in structure, not altogether unlike fine particles of molybdenite. The fracture is uneven, except in one direction, where there appears to be a cleavage. It is brittle and easily pulverised, and is not magnetic. It undergoes but little alteration before the blow-pipe, but becomes slightly magnetic. It is not acted upon in the slightest degree by hydrochloric acid, either hot or cold, but dissolves slowly and completely in nitric acid, when heated on a water-bath, without any liberation of free sulphur. Its sp. gr. is 5·01. It consists of chromium sesquisulphide and iron monosulphide. The analyses gave the following numbers:

	Found	FeS + Cr ² S ³
Sulphur	43·26	44·29
Chromium	36·38	36·33
Iron	20·36	19·38

100·00

100·00

Chantonay, Dép. de la Vendée, France. August 5, 1812.—Tschemmak (*Wien. Akad. Ber.* lxx. Nov. 1874) finds that the meteorites of Orvinio and Chantonay closely resemble each other in point of structure. Sections of the latter stone, of which representations are given in his paper, show it to be made up of chondritic fragments covered with a dark-coloured crust, and cemented together with a black and in places semivitreous material. The fragments are not very abundantly provided with spherules, although large ones are occasionally met with. The chondrite of this stone differs from that of the Orvinio meteorite in containing less iron; a section shows olivine, bronzite, a fibrous translucent material, as well as nickel-iron and magnetic pyrites; no chromite. Fine black veins of a mineral traverse the fragments here and there, and are connected with the cementing material. Similar veins are noticed in the meteorites of Sissa, Kakowa, Château Renard, Alessandria, and Pultusk; and in the Sissa and Kakowa stones they present the appearance as if the meteorite had originally come in contact with a molten material which had been injected into the clefts of its surface. Moreover, in the Chantonay stone, clefts are to be met with into which the black matter has penetrated to a depth of 6 mm. only, although the cleft remains partly open. The black semivitreous magma consists of an entirely opaque mass, enclosing flakes of the silicate which forms the fragment, as well as occasional spherules.

Although Rammelsberg, who analysed this stone, does not describe the physical character of the material he operated on, and did not examine the fragments and the cementing material separately, as Tschemmak has done in his examination of the Orvinio meteorite, Tschemmak points out that the two stones have much the same composition, and differ mainly in the proportion of iron. The characters observed in these two meteorites point to the conclusion that they did not originally possess their present constitution, but that they have attained their present appearance through the disintegration of a solid rock-mass and its subsequent cementation with a semivitreous magma. Though they resemble somewhat the eruptive breccias, they differ from them in that the meteoric cementing material is less homogeneous, and encloses compact flakes of the rock itself. The Chantonay stone exhibits the fine texture observed in some metamorphosed breccias. The two stones convey to us evidence of changes which must have occurred on the solid surface of some planet that was subsequently reduced to fragments (see the Orvinio Meteorite, p. 1293).

The Siderolite of Rittersgrün: found 1833 (*Nova Acta der k. Leop.-Carol. Deut. Akad. der Naturforscher.* xl. No. 8, 333, Halle, 1878). The examination by Winkler of the siderolite of Rittersgrün, Saxony, shows it to accord very closely in composition with the siderolite of Breitenbach in Bohemia, examined some years since in the Laboratory of the Mineral Department of the British Museum, and strengthens

the views expressed at the time that these bodies, as well as the meteorite of Steinbach in the Erzgebirge, were probably members of the same fall, possibly of the 'Eisenregen,' reported by Sarcetorius to have fallen 'im Meissnischen' at Whitsuntide 1164.

The Rittersgrün siderolite was found in 1833 by a workman employed in clearing the forest, and offered for sale as old iron to a smith, but without success; but in 1861 it came to the notice of Breithaupt, and was secured for the mineral collection of the Bergakademie of Freiberg. Its mean diameter is 0.43 meter, and its weight 86.5 kilog. It has recently been sawn through in Vienna, a troublesome and costly work extending over two months. An excellent chromolithograph of the surface thus exposed was prepared by Prof. Weisbach in 1876, and published with a few notes.

The meshwork of nickel-iron of the siderolite encloses the following minerals: troïlite, asmanite, bronzite, and chromite. The metallic portion constitutes about 51.06 per cent., and the non-metallic ingredients about 48.94 per cent. of the stone. The nickel-iron contains:

Fe	Ni	Co	Cu	P	S	Si	C	Asmanite
89.090	9.740	0.230	0.035	0.150	0.011	0.066	trace	0.056 = 100.278

which constituents may be arranged as follows:

Nickel iron, Fe ⁹ Ni	98.905
Iron nickel phosphide, (FeNi) ⁴ P	0.293
Iron phosphide, Fe ² P	0.539
Iron silicide, Fe ² Si	0.330
Iron sulphide	0.030
Iron carbide	trace
Copper	0.035
Asmanite	0.056
	<hr/>
	100.278

The iron sulphide, regarded as troïlite or monosulphide, when in the form of pieces, is not acted upon by the magnet, and when in the state of powder, but slightly so. The ratios of iron to sulphur in troïlite and in magnetic pyrites differ in so small a degree that the analytical results do not always set the question at rest. Moreover it is a question whether the meteoric sulphide, associated as it is with nickel-iron, does not contain some of that metal as an ingredient. The numbers obtained in these analyses are as follows:

	Calculated	I	Found II	III
Iron	63.63	65.87	63.58	63.00
Nickel	—	1.40	—	1.02
Sulphur	36.37	34.27	36.42	35.27
Silicic acid	—	—	—	0.67
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	101.54	100.00	99.96

The asmanite appears to have the density of 2.274—2.278, and the following composition:

	I	II
Silica	95.77*	97.84
Ferric oxide	3.16	1.65
Lime and magnesia	trace	—
Loss on ignition	1.07	1.01
	<hr/>	<hr/>
	100.00	100.50

As regards the crystalline form of this mineral, Weisbach considers that the recent researches of Schuster and of von Lasaulx have placed almost beyond doubt the identity of tridymite and asmanite. It occurred to Winkler that the relative solubility of tridymite and asmanite in potash-solution should be determined, and in as nearly possible parallel experiments as could be devised, and it was found that of tridymite from Siebenbürgen 49.63 parts, and of the asmanite of the siderolite from Rittersgrün 43.88 parts were dissolved.

The bronzite, the most important of the non-metallic minerals, was obtained in a pure state with comparative ease. It is but slightly affected by the blowpipe, and is not acted upon by acids, with the exception of hydrogen fluoride. Its sp. gr. is 3.310. It has the following composition:

* By difference.

	I	II	III
Silicic acid	57.27	56.56	56.56
Alumina	2.28	2.05	2.04
Ferrous oxide	10.99	10.74	10.09
Manganous oxide	0.41	0.42	0.55
Magnesia	24.78	25.13	25.59
Lime	1.77	2.52	1.66
Soda	not deter.	1.42	1.43
Chromite	0.94	0.98	0.98
	98.44	99.83	98.90

No trace of olivine was met with in this meteorite.

Heated in a vacuum, it lost 0.23 per cent. of its weight, and the gas evolved took fire, but was so small in quantity that it could not be further examined. The meteorite possesses the 'crust of fusion' in a well-developed form; it is of about the thickness of a piece of paper, and close under it are found the mixtures of the minerals troilite, asmanite, and bronzite of an unaltered light brown colour, although they turn deep black when raised to a temperature slightly above that at which lead melts.

Grosnaja, Banks of the Terek, Caucasus. June 28, 1861, 7 A.M. (*Mineralog. und Petrographischen Mittheilungen*, 1877, 153).—Some sixteen years ago Abich sent a description of this fall to G. Rose in Berlin. It appears that most of the stones fell into the Terek; one, however, which resembles a colossal hailstone, penetrated the ground to the depth of $1\frac{3}{4}$ feet, and was taken out while still warm. The crust was to a considerable extent removed; the density of the stone is 3.7. A report by the military authorities has recently been prepared, and it appears in Tschermak's paper, together with his notes on an examination of the stones.

The fall appears to have been attended with a great deal of noise, like the firing of cannon followed by a fusillade. The stone secured fell within 30 paces of the bank of the Terek. When taken out, it was found to weigh in all 10 lbs. Many heard a second sound, as though the meteorite burst twice in its descent through the atmosphere, and the noise attending the fall was heard 8 versts distant on the other side of the Terek. The water fizzed just as it would if brought in contact with a heated iron.

A system of cracks and fissures arrayed like the branches of a tree traverse the stone, giving the impression that they are the result of the blow which it received on its fall. The colour is blackish-grey with bright points. There are many enclosed mineral particles, some almost invisible, others 1 cm. across, the greater part having a diameter of less than 2 mm. The matrix is black and opaque, even when viewed in microscopic section, and many of the enclosed particles are opaque or only translucent in points. Most of these, however, are transparent, and the majority have a circular or rounded outline. Five distinct ingredients could be distinguished. The first is a clear greenish mineral, with incomplete cleavage along two directions, perpendicular to each other, and identified as olivine. A second in round tough spherules, brownish in hue, and not numerous, with a finely foliated or finely fibrous structure, was found to be bronzite. Enclosed particles are sometimes made up of these two minerals, sometimes, but not very frequently, of them together with a third silicate in long greenish prisms, which have the appearance and angles of augite. The meteorite also contains some magnetic pyrites (troilite?), a very little nickel-iron, and perhaps a little carbon, to which the dark hue of the matrix is due.

Two peculiarities observed in several chondritic meteorites are noticeable in this one. The first is the occurrence of a crust on the bronzite spherules possessing fibrous structure. This crust is thin, and is distinguished from the enclosed material by its paler colour; it has the same fibrous structure, doubly refractive power, and, in fact, is optically orientated like the enclosed silicate. It appears to have been produced by some agent acting from without, perhaps heat in conjunction with a reducing gas. The agent has not caused fusion, but a slight modification of the texture of the surface. The second peculiarity is the distribution in zones of the magnetic pyrites in many of the granular enclosed masses. When a section is examined by reflected light, it is found that many of these masses are apparently surrounded by a crust of the sulphide; in others it occupies the centre of the mass, in all cases apparently filling up interstices. It seems as if the sulphide had impregnated the rocky mass, and the absence of all magnetic pyrites in the very compact enclosed particles, and the tough fibrous bronzite chondra, confirms this view. It is believed that this impregnation took place after the enclosed mineral particles attained their present form, and the only explanation which can be suggested is that this must have happened while the whole tufaceous mass was strongly heated. The enclosed granules coming

in contact with fused magnetic pyrites must have drawn it into the fine fissures and interstices, in some instances into the cavities of the granules themselves. This implies the existence of two definite stages in the formation of these and similar chondritic structures : first, the production of the olivinous tuff by the splitting and attrition of the rock when the tougher particles are rolled and rubbed together till they have a roundish or spherular form ; and secondly a subsequent application of heat to the tuff, accompanied not unfrequently by the reducing action of gases and vapours.

The stone consists of :

SiO ²	Al ² O ³	FeO	CaO	MgO	K ² O	Na ² O	C	H	Magnetic pyrites	
33.76	3.44	28.86	3.22	23.55	0.30	0.63	0.68	0.17	5.37	= 100

Olivine appears to be the prevailing silicate of the meteorite. In addition to bronzite there appears to be a little augite and felspar.

Roda, Province of Huesca, Spain. Spring of 1871 (*Compt. rend.* lxxix. 1507 and 1509).—This stone fell at a spot two kilometers from Roda ; the exact date of its fall is not known. It is covered with a black crust ; the interior is ashy-grey with greenish grains resembling peridot, some several mm. in diameter, scattered throughout the mass. The grey surface is, however, not of a uniform tint, but presents two irregularly-shaped areas, one grey, the other yellowish-grey. The stone is very friable. Before the blowpipe it is fusible, becoming black and feebly magnetic.

Only 14.75 per cent. of the stone is acted upon by acid, the portion unacted upon amounting to 85.97 per cent. Below are given, in addition to the composition of the constituents separated by acid, the results of an analysis of the minerals constituting the mass of the stone :

	SiO ²	Al ² O ³	Cr ² O ³	FeO	CaO	MgO	K ² O	Na ² O	S	
A. Soluble.	38.85	4.81	--	24.27	8.21	23.86	—	—	—	= 100.00
B. Insoluble.	52.93	1.95	0.39	16.29	1.92	26.52	--	--	--	= 100.00
C. Total.	51.51	2.30	0.34	17.04	2.31	26.61	0.80	0.40		= 101.31

The soluble portion appears to be an iron olivine, mixed probably with a little anorthite ; the insoluble portion, consists chiefly of bronzite, or, according to Pisani, probably hypersthene, with the specific gravity of which mineral that of the meteorite more closely accords. The sulphur and chromium are, it is presumed, present as magnetic pyrites and chromite ; no nickel whatever was detected.

The yellowish grains are very slightly attacked by acid, only 6 per cent. being soluble in that reagent. Their composition proved to be :

Silica	51.10	27.3
Alumina	2.83	1.3
Ferrous oxide	27.70	11.1
Magnesia	17.20	3.8
		98.83	43.9

These numbers indicate, according to Pisani's view, the presence of a hypersthene rather than a bronzite, a hypersthene richer in iron than that of Farsund, Norway. The ratio of iron oxide to magnesia is the same as that of the bronzites of the Hainholz, Shalka, Borkut, and several other stones.

On some grains of the mineral a well-marked cleavage was distinguished along one direction ; in others a disposition to cleave along a second direction was remarked ; on examining such fragments in the polarising microscope, however, one of the optic axes was almost always seen, while the other is invisible. The angle of the optic axes, as measured in oil, was approximately determined, making $2H = 104^\circ$. The bisectrix is negative ; but whether it was the acute or obtuse bisectrix was not determined.

Daubrée's examination points to the chief constituent of this stone being bronzite rather than hypersthene. The absence of dichroism, the frequent occurrence of the right angle in the contour of the crystals, and the fineness of the striae peculiar to bronzite, were noticed. Magnified 800 diameters, most of the crystals are seen to enclose yellowish-brown rarely translucent matter with very varied contour, and occasionally with a crystalline form, that of a modified oblique prism, which is that of pyroxene. They are ranged in rectilinear series, which are not always orientated parallel to the axes of the crystal. The Roda meteorite, with the single exception that it contains no iron, bears a great likeness to the meteorite of Lodran (1868, October 1), and establishes a new link between cosmical rocks and those belonging to our planet. If, says Daubrée, we were to refuse to admit the testimony of those who affirm that they witnessed the fall of this fragment of rock, the characters of its crust would fully attest its cosmical origin.

Orvinio (formerly Canemorto), near Rome. 1872, August 31, 5.15 A.M. (*Compt. rend.* lxxv. 655; G. S. Ferrari, *Ricerche fisico-astronomiche intorno all'Uranolito caduto nell'agro Romano*, Rome, Tip. Bel. Arti. 1873; P. Keller, *Pogg. Ann.* cl. 171; *Min. Mitth.* 1874, 258; M. Le Chev. Michel-Etienne de Rossi and G. Bellucci, *Atti del Acc. pontif. di Nuovi Lincei*, 1873; *Les Mondes*, Dec. 25, 1873; L. Sipöcz, *Min. Mitth.* 1874, 244; G. Tschermak, *Sitz. Ak. Wiss. Wien.* lxx. Novem. 1874). A meteor was seen at daybreak in the provinces of Rome, Umbria, Abruzzo, and Terra di Lavoro. It resembled a large red star, increasing in brilliancy as it travelled northwards, and leaving a white train. Two reports were heard, the second over Orvinio, where the greater part of the stone fell. Six fragments were found, weighing collectively 3.396 kilog. In September 1873 two more small fragments were heard of at Anticoli Corradi.

The mass of the stone is of a lead-grey colour; the ground-mass appears to be made up of two minerals, one clear and uniform, the other dull and less homogeneous. The stone acts powerfully on the magnet.

In the paper of M. le Chevalier Michel-Etienne de Rossi analyses of the stone are given, according to which it contains 16.34 per cent. of alumina and some arsenic. This is far in excess of that found in any other meteorite, and in the absence of a second and confirmatory analysis may be assumed to consist in part of magnesia thrown down with the alumina through the employment of insufficient ammonium chloride. The occurrence of arsenic is of extreme rarity; it is stated to be present in the iron of Braunau and the olivine of the Atacama meteorite.

Tschermak finds, on cutting this stone, that its structure is unusual and remarkable, consisting of light-coloured fragments (I) surrounded by a compact dark cementing material (II). The former are yellowish-grey, enclose spherules and particles of iron and magnetic pyrites, and are in fact normal chondrite, and resemble the mass of the stone which fell at Seres, Macedonia (June 1818). The latter enclose numerous particles of iron and magnetic pyrites, for the most part uniformly distributed; the portion nearest the enclosed fragments bears very distinct indications of having been at one time fluid, and conveys the impression that this cementing material was at one time in a plastic condition while in motion. Both parts have nearly the same density, and apparently the same chemical composition and mineral characteristics. The Orvinio stone resembles certain brecciated volcanic rocks, which consist of a ground-mass through which granular fragments of the same rock are distributed, as when older crystalline lavas are interpenetrated by others more compact and of a more recent date.

The meteoric rocks possessing chondritic structure are regarded by Tschermak as tufas which have undergone detrition, and their spherules as particles which, by their superior toughness, have acquired a rounded form during the trituration of the rock, instead of breaking up into splinters.

The dark-coloured cementing material contains two ingredients: an opaque semi-vitreous constituent, and particles in every way similar to the dark crust of the fragments from which they may probably have been detached; many of them can still be recognised as olivine and bronzite.

The two species of rock, the chondritic fragments with the sp. gr. 3.675 (I), and the darker cementing material, with the sp. gr. 3.600 (II), have the following composition:

	SiO ²	Al ² O ³	Cr ² O ³	FeO	MgO	CaO	Na ² O	K ² O	Fe	Ni	S
I. 38.01	2.22	trace	6.55	24.11	2.33	1.46	0.31	22.34	2.15	1.94	= 101.42
II. 36.82	2.31	trace	9.41	21.69	2.31	0.96	0.26	22.11	3.04	2.04	= 100.95

These analyses establish the similarity in composition of the two portions.

Castralia, Nash County, N. Carolina (*Sill. Am. J.* [3], viii. 147). May 14, 1874, 2.30 P.M.—A dozen or more stones fell, and although the fall took place by day, a luminous meteor was observed. The area over which the fragments fell was ten miles long by three wide. Three stones weighing 7.3 kilog. were found. The colour of the interior is in many parts a dark grey, owing to the presence of a large amount of nickel-iron; in the lighter portions are seen some white spots of a mineral which is doubtless enstatite.

The metallic part, 15.21 per cent., consists of:

$$\text{Iron} = 92.12; \text{nickel} = 6.20; \text{cobalt} = 0.41 \quad = 98.73$$

and the siliceous portions:

	SiO ²	Al ² O ³	FeO	MgO	Na ² O	S
A. Soluble	38.01	0.46	17.51	41.27	—	1.01 = 98.26
B. Insoluble	52.61	4.80	13.21	27.31	1.38	— = 99.31

The soluble silicate is an olivine in which the ratio of MgO to FeO is about 4 : 1; the insoluble part is a bronzite; and in addition to the minerals already mentioned,

the presence in the Castralia stones of small amounts of iron sulphide and anorthite was recognised.

Iowa County, State of Iowa (*Sill. Am. J.* ix. 459; x. 44, 206, 357; xi. 253). February 12, 1875; 10.30 A.M. (Chicago time).—*An Account of the Detonating Meteor of February 12, 1875*, by C. W. Irish, Iowa City, 1875; Delafontaine, *Bibliothèque Universelle*, Oct. 1875, 188; G. A. Daubrée, *L'Institut*, 1875 (Nos. 105-122); C. W. Gümbel, *Münch. Akad. Ber.* 1875, v. 313. A great number of large stones fell on this occasion, weighing in all 700 lbs., the largest being 120 lbs. in weight. Some passed so near the earth's surface that they clipped off the branches of trees. Three separate explosions of the fire-ball were noticed while still in view, and about two or three minutes after it had disappeared, three reports, resembling the discharge of the blast of a quarry, were heard.

The stones have the usual black crust. A preliminary chemical examination showed them to contain:

Nickel-iron = 12.53; troïlite = 5.82; silicates = 81.64 = 100.00

The nickel-iron consists of:

Iron = 89.04; nickel = 10.35; cobalt = 0.54 = 99.93

with traces of copper, phosphorus, and sulphur. The silicate contains iron, ferrous oxide, alumina, magnesia, and soda, with traces of lithia and potash, and is very similar in composition to a large class of meteorites notably represented by the stones which fell at Vouille (May 31, 1831), and Aumale, Algeria (August 25, 1865).

A. W. Wright collected and analysed the gases contained in this meteorite and arrived at the following results:

	I	II	III	IV	V
	At 100°	At 250°	Below red-heat	At low red-heat	At full red-heat
Carbon dioxide	95.46	92.32	42.27	35.82	5.56
Carbon monoxide	0.00 (?)	1.82	5.11	0.49	0.00
Hydrogen	4.54	5.86	48.06	58.51	87.53
Nitrogen (calculated),	0.00	0.00	4.56	5.18	6.91
	100.00	100.00	100.00	100.00	100.00

The reader is referred to the *Amer. Jour. Sc.* for the papers subsequently published by Mallet and Wright on the question of the conditions under which gases are occluded by meteorites.

Prof. Gümbel finds the crust of this meteorite to possess a deep bottle-green or brownish-red colour, and to exhibit in polarised light all the characters of an amorphous vitreous mass. The composition of the stone, according to his analysis, is:

Meteoric iron	12.32
Troïlite	5.25
Silicate, decomposed by acid	48.11
Silicate, not acted upon by acid . . .	34.32
	100.00

The silicate decomposed by acid is an olivine, having the formula $2(\frac{3}{2}\text{MgO} \cdot \frac{1}{2}\text{FeO}) \cdot \text{SiO}_2$, and the insoluble silicate gave the oxygen ratios: Silicic acid = 29.68; bases = 10.92. It appears not improbable that the silicate in this case was not completely decomposed during fusion. A plate accompanying Gümbel's paper shows a microscopic section of the meteorite exhibiting olivine, augite, meteoric iron, chromite, troïlite, particles of a reddish hue which resemble garnet, but refracting light doubly, and possessing optical characters which will not allow of their being identified with nosean; also chondra showing fibrous, radiate, and granular structure, as well as others which evidently consist of olivine, and some which are opaque and finely granular. The meteoric iron has a hackly angular structure, and such an appearance as it would present if reduced to the metallic state in the position which it at present occupies.

Zsádány, Temesvár, the Banat, Hungary. March 31, 1876 (*Egyetértés és Magyar Ujság*, April and June, 1875; *Verhand. Naturhis. Med. Vereins zu Heidelberg*, 1878, ii. Heft. 2).—No meteor was seen; a sound as of platoon-firing was heard; and a small shower of black stones fell, some of which were cold when picked up. Sixteen stones in all were found, having an aggregate weight of 400 grams.

The finely-grained light-grey matrix encloses granules of magnetic pyrites (troïlite?), granules and plates of nickel-iron, and numerous dark-grey crystalline spherules, averaging $\frac{1}{2}$ mm. in diameter; one little sphere had a breadth of $3\frac{1}{2}$ mm. They had an excentric-radiate or contorted-radiate structure. A freshly broken surface of the

stone is studded with these chondra, and they are easily removed from the matrix. As regards their mineralogical aspect, the spherules are found to be of two kinds. One consists of small prisms of a rhombic mineral which has all the appearance of a variety of enstatite; others are found to possess the characters of olivine. An accessory mineral, transparent, pure, and with well-defined edges, differs from the rhombic augite in exhibiting no cleavage fissures, from olivine by the smoothness of its polished exterior, and from both of them by exhibiting distinct pleochroism with absorption, one tone being colourless, the other pale-red with a faint tinge of brown. It appears to be rhombic, and shows a close resemblance to a variety of hypersthene found by Cohen in a gabbro from S. Africa. The Zsádány stone resembles those which fell on different occasions at Laucé, Gopalpur, and Pultusk.

The portions soluble and insoluble in acid have the following composition:

	Soluble portion	Insoluble portion
Silica	44.56	56.71
Alumina	trace	2.32
Iron oxide	17.54	13.21
Lime	trace	1.77
Magnesia	37.90	25.99
	100.00	100.00

The stones appear to consist to the extent of three-fourths of a bronzite, the remaining fourth being an olivine in which the equivalents of MgO : FeO are as 3.89 : 1, or approximately that which is often met with in meteoric olivines.

Feid-Chair, Corde de la Calle, Constantine. August 16, 1875 (about noon) (*Compt. rend.* 1877, lxxiv. 70).—This meteorite fell at a spot named Feid-Chair, about 30 kilometers from La Calle, the descent being attended with the customary luminous appearance. It weighs 380 grams; all search to discover other stones proved of no avail. The stone has a black crust and a grey interior, in which particles of nickel-iron and troilite are imbedded. Spherules are recognised, but the matrix likewise exhibits a brecciated structure; grains of a dull black hue are also distributed through the mass. The Feid-Chair meteorite closely resembles the stones which fell at La Baffe (Sept. 13, 1822), Herodia, Costa Rica (April 1, 1857), Canellas, near Barcelona (May 14, 1861), and Khetree, Rajpootana (Jan. 19, 1867).

Rowton, near Wellington, Shropshire. April 20, 1876; 3.40 P.M.—A block of meteoric iron, weighing 7½ lbs., was seen to fall at this place. Rain was falling heavily at the time, when a strange rumbling noise was heard, followed by a startling explosion like a discharge of heavy artillery, audible over an area several miles in extent among the neighbouring villages of Shropshire. The iron was found about an hour later; the hole it had made was probed, and it was discovered about 18 inches below the surface. The hole was nearly perpendicular, the meteorite having entered the ground almost vertically in a N.W. to S.E. direction, and when found it was quite warm. The mass is irregularly angular, and except at the point where it struck the ground, it is covered with a thin pellicle of magnetic oxide of iron. It was presented by the Duke of Cleveland to the British Museum. It is only the seventh aërosiderite, or meteoric iron, the fall of which has been witnessed, although upwards of a hundred iron masses have been discovered in different parts of the globe, which are undoubtedly meteoric, and two such have been found in Great Britain.

No analysis of this iron has yet been published.

Vavilovka, Gov. Cherson, Russia. 1876, June 7th (*Mém. de la Soc. nation. des Sciences nat. de Cherbourg*, xxi. 205).—It appears that at this time a large number of stones fell, and a noise as of thunder was heard. A stone examined by R. Prendal had a black crust 0.6–1.0 mm. thick, and a number of irregular and prominent bands. A cut section showed under a glass a fine-grained grey mass through which numberless white spots with angular boundaries are distributed. This meteorite is so brittle that the preparation of sections was attended with great difficulty. The metallic constituents are particles of nickel-iron distributed throughout the mass of the stone, and grains of a sulphide which are not magnetic. The specific gravity of this meteorite is 3.51, and an analysis by R. Prendal shows it to contain:

SiO ²	FeO ²	Al ² O ³	CaO	MgO	Alkalies	Iron sulphide	Ni
63.81	9.41	8.75	2.07	18.54	1.14	5.26	0.70 = 99.68

These numbers throw but little light on the minute constitution of the stone. It is to be classed with the chondrites.

Ståldalen, near Kopparberg, Örebro län, Sweden. June 28, 1876; 11.50

A.M. (*Föredrag i Mineralogi vid Akademiens årshögtid den 3 April, 1877; Aftonbladets Artiebologs Tryckeri*, Stockholm, 1877; *Nature*, July 19, 1877; *Öfversigt af Kongl. Vetenskaps Akad. Förhandl.* 1877, No. 4, p. 35). A meteor traversed the greater part of Central Sweden in a W.N.W direction, and was plainly visible in very bright sunshine. A loud whistling noise was heard, followed by two sharp reports and others less loud resembling thunder. The fall of the meteorites was witnessed by eight or ten persons. The largest weighs $4\frac{1}{2}$ skulpund (1 lb. av. \pm 1.068 ltt. or skulpund). Ståldalen is a station on the Swedish Central Railway! Some of the meteorites which fell into the water were lost. The total number of stones found is eleven, and they weigh collectively 34 kilog. Lindström finds the total composition of one of these stones to be:

Silica	35.71	Soda	0.62
Phosphoric acid	0.30	Potash	0.15
Alumina	2.11	Iron	21.10
Chromium oxide	0.40	Nickel	1.61
Ferrous oxide	10.29	Cobalt	0.17
Manganous oxide	0.25	Phosphorus	0.01
Nickel monoxide	0.20	Sulphur	2.27
Lime	1.61	Chlorine	0.04
Magnesia	23.16		
			100.00

Of these ingredients, 4.51 per cent. constitute magnetic pyrites (?), and 14.65 per cent. nickel-iron, the composition of which appears to be:

Fe	Ni	Co	P
90.78	8.29	0.88	0.05 = 100.00

The portions (I) gelatinisable with and (II) unacted upon by acid have the following composition:

	SiO ^a	P ² O ^a	Al ² O ^a	FeO	NiO	MnO	CaO	MgO	Na ² O	K ² O	Cl
I.	36.76	0.83	0.13	20.35	0.60	—	0.64	40.47	0.18	0.16	9.13 = 100.25
II.	67.37	0.07	5.07	8.03	—	0.63	3.41	23.54	1.38	0.23	— = 99.73

In the soluble portion the oxygen-ratio of acids to bases is 20.08 : 21.16, and in the insoluble part 30.64 : 15.08. In addition to olivine and bronzite, this meteorite appears to contain an insoluble felspar and a little apatite.

Rochester, Indiana. 1876, December 21, 9 P.M. (*Sill. Am. J.* [3], xiv. 219).—The course of this meteor was studied by Professor Kirkwood of Bloomington, Indiana, who considers the length of its observed track to be from 1000 to 1100 miles, one of the longest on record. Its height is supposed to have been 38 miles above the place where the fragment preserved fell from it. In various parts of its track it threw off fragments, accompanied with the usual rumbling noise. 'The pyrotechnic display is said to have been transcendently beautiful, hardly equalled or surpassed by any previous occurrence of the kind.' The only fragment preserved fell at Rochester and rebounded, falling finally on the surface without penetrating it. 'It is of the pisolitic variety, very friable, of a grey colour, easily crushed under the fingers into light powder and small globules, some of them *perfectly spherical*, of which the writer has some specimens 2 mm. in diameter.' It resembles the Aussun stone. The crust is dull black and quite rough. The composition of the stone appears to be approximately:

Bronzite and pyroxene minerals	46.00
Olivine minerals	41.00
Nickel-iron	10.00
Troilite	3.00
Chromite	0.15

and that of the portion soluble (I) 47.80 per cent., and insoluble in acid (II) 52.20 per cent.:

	SiO ^a	FeO	Al ² O ^a	CaO	MgO	Cr ² O ^a	Na ² O
I.	34.55	27.75	—	—	36.38	—	0.46 = 99.14
II.	67.81	11.04	0.23	5.31	24.97	0.10	0.84 = 100.30

The spherules were isolated and examined; they contained 46.80 per cent. soluble silicate, and 53.20 insoluble silicate, the magnesia in the soluble part amounting to 34.48 per cent.; they are consequently merely concretions of the matrix of the stone. The nickel-iron contained:

Iron = 94.49; Nickel = 4.12; Cobalt = 0.51	= 99.12
--------------------------------------------	---------

Warrenton, Missouri. 1877, January 3 (about sunrise) (*Sill. Am. J.* [3],

xiv. 222).—A sound was heard like the whistle of a locomotive, or like the passage of a cannon-ball through the air; it came from the north-west, and became louder and louder to four observers stationed at Warrenton. On looking up they saw a falling object strike a tree, breaking off the limbs and then coming to the ground with a crash. The stone was broken in pieces. It was supposed to have had a conical form and a length of 18 inches; the weight was estimated at 100 lbs., but only 10 to 15 lbs. weight of the fragments have been saved. No explosion or luminous phenomena were observed. It most closely resembles the Ornans stone (July 11, 1868). Its crust has an unusual thickness, being in places $2\frac{1}{2}$ to $3\frac{1}{2}$ mm. thick. The interior of the stone has a very dark uniform ash colour; it is soft and easily crushed, and has a specific gravity of 3.47.

The ratio of the constituent minerals is:

Olivine minerals	76.00
Bronzite and pyroxene minerals	18.00
Nickel-iron	2.00
Troilite	3.50
Chromite	0.50

80.40 per cent. of silicate is soluble in acid and has the composition under I; 19.60 per cent. of silicate, being insoluble in acid; it is given under II.

	SiO ^a	FeO ^a	Al ^a O ^a	CaO	MgO	Na ^a O	NiO	CoO	Cr ^a O ^a	
I. Soluble.	33.02	37.57	0.12	trace	28.41	0.07	1.54	0.31	—	= 101.04
II. Insoluble.	56.90	10.20	0.20	7.62	22.41	1.00	—	—	0.33	= 97.66

The nickel-iron contains:

$$\text{Iron} = 88.51; \text{Nickel} = 10.21; \text{Cobalt} = 0.60 \quad = 99.32$$

Cynthiana, Kentucky. 1877, January 23, 4 P.M. (*Sill. Am. J.* [3], xiv. 224). A brilliant meteor was seen traversing Monroe County, Indiana, in a south-easterly direction; it was also observed at Decatur County, of the same state. The meteorite fell about sixty miles distant from these places, and appeared to descend almost vertically, accompanied with the usual noises. One mass was seen to fall, and was dug out of a hole thirteen inches deep. This stone is wedge-shaped, with one portion of it very extensively and regularly pitted, the rest being smooth. The crust is dull-black and perfect as when it fell. The stone weighs six kilograms; it is of the harder brecciated variety, and when broken presents a mottled surface identical with that of the Parnolle stone, which it resembles in every respect, even in density, which in both cases is 3.41. The constituent minerals of the meteorite appear to be:

Olivine minerals	50.00
Bronzite and pyroxene minerals	30.00
Nickel-iron	6.00
Troilite	5.50
Chromite	0.52

The silicates soluble in acid form 56.50 per cent. of the total silicates, and possess the composition given under I; those insoluble in acid amount to 43.50 per cent., and are given under II:

	SiO ^a	FeO	Al ^a O ^a	CaO	MgO	Na ^a O	Cr ^a O ^a	
I. Soluble.	33.65	30.83	0.11	trace	34.61	—	—	= 99.20
II. Insoluble.	57.60	11.42	0.43	5.70	23.97	1.24	0.38	= 100.74

The nickel-iron forming 5.93 per cent. of the meteorite consists of:

$$\text{Iron} = 90.64; \text{Nickel} = 8.35; \text{Cobalt} = 0.73 \quad = 99.72$$

Hungen, between Steinhelm and Borsdorf, Province Oberhessen. 1877, May 17, 7 A.M. (*Min. Mitth.* 1877, 313).—An eyewitness of the fall of one of these meteorites states that, as he was passing through a wood, he heard a noise as of thunder, followed by a humming, hissing, whistling sound, such as would be caused by a number of stones quickly rushing among trees. One struck a pine tree close to him, severed a branch about the thickness of the finger, and fell at his feet. Buchner visited the spot five months later, and found a second stone weighing 26 grams. The first weighed 86 grams. The descent of the meteorite took place in the direction from north-west to south-east. The crust of this stone is dull black and thin; the fractured surface displays a grey, occasionally brown matrix, traversed by a very thin but very conspicuous brilliant black band of material; it runs obliquely to the flattened side of the stone, and is also found in the smaller mass picked up five months

later, which evidently never formed part of the larger meteorite. On part of the fractured surface of the larger stone a second black line, parallel to the first but less brilliant, is seen. Abundant particles of nickel-iron and troilite are met with; the crust appears to consist, to the extent of one half, of the metallic alloy. The ground-mass appears to be olivine; some olivine spherules are conspicuous, surrounded by the black material or by nickel-iron; other chondra have a banded or radiated structure, as in the stones of Shergotty or Gopalpur, and appear to be bronzite; and lastly there are spherules of a homogeneous gray translucent substance, devoid of or rarely traversed by fissures.

According to Tschermak's examination of the smaller stone, it approaches closely in its character to the Pultusk meteorites. The black crust has the unusual thickness of 1.5 mm., and encloses nickel-iron, magnetic pyrites (troilite?), and even lustreless chondra which may consist of chromite or picotite. Tschermak also determined the presence of granules of olivine, bronzite, and diallage, for such he believes to be the brown mineral, forming angular fragments, which are found not to be rhombic and to resemble an augite.

Cronstadt, Orange River Free State, South Africa. 1877, June.—A shower of stones fell near Cronstadt in June 1877, in a wooded district, so that few could be collected. One of them is preserved in the British Museum.

Soko-Banja, N.E. of Alexinatz, Servia. 1878, October 13, about 2 P.M. (*Verhandl. der k. geolog. Reichsanstalt*, 1877, 328; *Deut. Chem. Ges. Ber.* 1878, xi. 96).—Two explosions, like salvos of artillery, were heard, accompanied by a brilliant display of light, such as attends the bursting of shells. This noise lasted some time, and was followed by a sound resembling the firing of musketry. Soon after the explosions a number of meteorites fell to the ground, over an area $1\frac{1}{2}$ mile in length and half a mile in breadth. The total weight of material which fell amounted to 80 kilograms.

All the meteorites are covered with a black rough vitreous crust 0.5 mm. in thickness, and exhibiting numerous depressions; the interior consists of spherules of various sizes, some brown, some yellow, cemented together by an ash-grey material, and presenting the appearance of a trachytic lava. The sp. gr. of the stone is 3.502. The meteorite consists of:

	I	II
Nickel-iron	3.8	3.7
Silicates	96.2	96.3
	<hr/> 100.0	<hr/> 100.0

A fragment of nickel-iron was found to consist of:

Iron = 78.13; Nickel = 21.70; Copper = 0.17 = 100.00

This is a high percentage of nickel; the ratio of the metals is Fe : Ni = 4 : 1. The iron sulphide is monosulphide containing 63.84 per cent. of iron; theory requires 63.64 per cent. The portion acted upon by acid (I) and withstanding that reagent (II) consisted of:

	I	II
Silicic acid	32.24	56.66
Iron protoxide	28.41	23.55
Manganese oxide	0.20	0.003
Magnesia	30.53	20.84
Soda	0.43	—
Potash	0.09	—
Iron	0.70	—
Nickel	0.17	—
Iron monosulphide = 6.78	{ Fe = 4.31 S = 2.47	—
Chromite	—	0.11
Phosphorus	—	trace
	<hr/> 99.55	<hr/> 101.163

Neither alumina nor lime appears to be present, and felspathic and augitic constituents are consequently absent. The oxygen present in the two silicates amounts to—

	I	II
Silicic acid	17.19	30.22
Iron protoxide	6.31	5.23
Magnesia	12.21	9.33
	<hr/> = 18.52	<hr/> = 14.56

The soluble portion is therefore an olivine having approximately the composition

represented by the formula $2(\frac{3}{4}\text{MgO}, \frac{1}{4}\text{FeO}), \text{SiO}_2$; and the insoluble portion a bronzite of the form $(\frac{3}{4}\text{MgO}, \frac{1}{4}\text{FeO}), \text{SiO}_2$; the ratio of iron oxide to magnesia being the same in both silicates.

Meteorite from Tieschitz, Moravia. July 15, 1878; 1.45 P.M. (*Wien. Akad. Denkschriften. Math.-naturwissenschaft. Classe xxxix.* Nov. 21, 1878).—A stone fell at this date, with the usual accompanying noise, within 100 paces of some people whose attention was directed to a small dark cloud from which a peculiar and ever increasing noise proceeded. This cloud was suddenly seen to become incandescent, but in no very high degree, and the noise became still louder, when a body was seen to fall from the cloud. The stone was warm when found. The noise was heard in the neighbourhood two miles around. The stone was secured, and was sent on the 19th to the Museum of the Technical High School of Brünn. The meteor appears to have passed over Daubrawic and Sloup, and the path to have been through Azimuth 108° altitude 40° , and the apparent radiant in R A 68° , declination 40° .

This stone only was found, and all search for others was in vain. The stone weighs 27.5 kilog., and has the form of an irregular pyramid with an almost rectangular base. The entire surface is covered in places with a black crust, of about the thickness of that found on the stones which fell at Pultusk; on the large convex side, which is called the 'breast side,' it is much thinner, and exhibits a radiated character. On the back it is thicker and rougher, and without a trace of the radiated structure. The 'breast-side' is free from all great depressions, while the others show them, due probably in part to the original form of the stone, partly to the action of currents of air on the surface when melted. The freshly broken surface of the stone is dull, ash-grey in hue, darker than the Pultusk stone, the texture finer and more sharply marked than in the case of most of the chondrites. It exhibits many small dull grey or dark coloured chondra, and splinters and fragments of the same kind, many larger dull-grey chondra, also white small chondra, and white fragments, the latter much fewer than the former. Between them are an ash-grey earthy matrix and very few yellow metallic lustrous particles. Most of the dark chondra are less than 1 mm. in diameter; those which have a diameter of 1 mm. are fewer, and there are occasional chondra which exceed 1 mm. in size. The largest one had a diameter of 5 mm.

The microscopic examination of the sections of this meteorite displayed many curious features, and appeared to confirm the views already put forth by Tschermak regarding the probable influences which have taken part in the form which the chondra and other enclosures take. Some chondra present an appearance which has not hitherto been observed. They have round depressions, which point to a plasticity of the chondra during contact, as if the spherules had acquired their shape during the act of rubbing which formed the splintered fragments. Others, again, have projections of a rounded form or an almost pointed end. These chondra are the result of volcanic eruption or explosion.

Olivine.—Both in the matrix and in chondra well-developed crystals of olivine are to be met with. They have the same form as the olivine in basalt. Many of the chondra consist of individual crystals. Many crystals have cavities, enclosing black angular grains, or a black impregnation of the crust, or black, slightly translucent spherules or enclosures of 'glass'; some exhibit a most distinct surface of the enclosed material.

Bronzite.—Barred and fibrous individuals of a brown colour are regarded as bronzite. Some of the barred chondra, shown in the plate accompanying the paper by Makowsky and Tschermak, are very perfectly developed and are very curious. Some have a dark border, others a light rim. In these chondra, also, the enclosed material already referred to is met with.

Enstatite.—Many of the chondra of this mineral are distinguished by their marked foliated structure. The enclosed 'glass' is also found in them. Many spherules, and fragments of spherules, of a crystallised mixture of bronzite and olivine, and of enstatite and olivine, were noticed; none, however, of a crystallised mixture of enstatite and bronzite; and it appears, therefore, as if the meteoric tuff originated from two sorts of stony mixtures.

Augite.—A few small chondra, with a compact pale-coloured crust, have a texture and colour which differ from all the foregoing. The entire spherule is shown by polarised light to be an individual; the crust is almost colourless, the interior has a brownish-green hue. Their reaction with light points to their being augite.

Magnetic Pyrites and Nickel-iron.—Magnetic pyrites occurs as grains enclosed in the other chondra and splinters of chondra as well as free in the matrix. The nickel-iron is, for the most part, in the form of irregular particles, with a hackly surface in

the matrix. In some of the spherules, both magnetic pyrites and nickel-iron have a distinct concentric arrangement.

The stone of Tieschitz belongs to that division of the chondritic meteorites which Tschermak some years ago classified as remarkable for 'many brown, finely-fibrous chondra.' The sp. gr. of the stone is 3.59. It contains about 85 per cent. of non-metallic minerals. No trace of any mineral resembling a felspar could be detected. The percentage composition of the stone is as follows :

	Olivine	Bronzite and Enstatite	Augite	Magnetic Pyrites	Nickel iron	Totals (calc.)	Totals (anal.)
SiO ₂	13.99	18.84	7.90	—	—	40.73	40.23
Al ₂ O ₃	—	—	2.09	—	—	2.09	1.93
FeO	13.86	5.47	0.73	—	—	20.06	19.80
MgO	10.94	9.53	0.61	—	—	21.08	20.55
CaO	—	—	1.42	—	—	1.42	1.54
Na ₂ O	—	—	1.26	—	—	1.26	1.53
Fe	—	—	—	2.46	7.97	10.43	10.26
Ni	—	—	—	—	1.31	1.31	1.31
S	—	—	—	1.62	—	1.62	1.65
	38.79	33.84	14.01	4.08	9.28	100.00	

or

Olivine	38.79
Bronzite and enstatite	33.84
Augite	14.01
Magnetic pyrites	4.08
Nickel-iron	9.28

100.00

Esterville, Emmet County, Iowa. 1879, May 10, 5 P.M. (*Amer. Jour. Sc.* xviii. 77).—A meteor exploded over this spot, and was seen to fall in full daylight. One fragment, weighing 500 lbs., fell on railroad land, and was dug up from a depth of 14½ feet in a stiff clay soil. Another portion, weighing 170 lbs., fell at a distance of two miles from the first. Many smaller pieces, of a few ounces or pounds weight, were scattered in the vicinity. The smaller mass fell upon a dry knoll, and penetrated the earth vertically to a depth of 4½ feet. The fall was accompanied by a noise described as a continuous roll of thunder accompanied by a crackling sound. The stone has been placed in the hands of Prof. C. W. Hall, of the Minneapolis University, for complete investigation. The preliminary examination points to the metallic portion consisting of an alloy of iron, nickel and tin. Full half the mass consists of stony matter, which appears in dark green crystalline masses imbedded in a light grey matrix. When the whole is powdered a violent reaction ensues on addition of hydrochloric acid, which is increased by boiling. The boiling acid appears to dissolve all but the grey matrix. Some of the crystalline masses are two inches thick, and exhibit distinct monoclinic cleavage. Under the microscope, in thin sections, olivine and a triclinic felspar appear to be imbedded in a matrix of pyroxene. The iron shows the Wiedemannstättian figures very finely.

W. F.

On the Gases occluded in Meteorites (CO, CO₂, CH₄, H, N), see A. W. Wright (*Sill. Am. J.* [3], ix. 459; x. 44; xi. 253; xii. 165; *Jahresb. f. Chem.* 1875, 1312, 1315; 1876, 1312).

METHACRYLIC ACID, C⁴H⁶O² = H²C=C(CH³).CO²H, or, according to Fittig, =CH—CH(CH³)—CO²H (*Liebig's Annalen*, clxxxviii. 95). This modification of crotonic acid, which Frankland and Duppa first obtained by acting on ethylic dimethoxalate with phosphorus trichloride, and saponifying the resulting ethylic ether with potash (vi. 825), is also produced by dissolving citraconic acid or anhydride, or mesaconic acid, in fuming hydrobromic acid—or by heating citraconic anhydride or mesaconic acid with strong hydrochloric acid—and boiling the resulting citra- or mesa-, bromo- or chloro-pyrotartaric acid with concentrated soda-ley, e.g.:



This decomposition of citrabromo-pyrotartaric acid affords the means of preparing methacrylic acid in large quantity (vi. 511–587). See also Fittig (*Liebig's Annalen*, clxxxviii. 42).

Methacrylic acid appears to occur in small quantity in the portion of the product of saponification of Roman cummin-oil (consisting chiefly of isobutyric acid) which distils at 160° (Fittig, *Deut. Chem. Ges. Ber.* x. 513).

On the conversion of Methacrylic Acid into Isobutyric Acid by the action of Sodium-amalgam, and into Iodisobutyric Acid by solution in fuming Hydriodic Acid, see p. 587 of this volume.

Methacrylic acid dissolves easily also in fuming *hydrobromic acid*, even at 0°, the solution, after some time, depositing a crystallised addition-product, and almost at the same time a thick oil, which is formed by polymerisation, and solidifies over sulphuric acid and potassium hydrate to an amorphous resinous mass (L. Paul, *Ber.* ix. 122).

METHANE, CH₄. This hydrocarbon is formed when a mixture of carbon oxide and hydrogen is exposed to the action of electricity in an induction-tube: $\text{CO} + 3\text{H}^2 = \text{H}^2\text{O} + \text{CH}^4$ (Brodie, *Proc. Roy. Soc.* xxi. 245); also by the action of zinc-powder on chloroform dissolved in aqueous alcohol: $2\text{CHCl}^3 + 3\text{H}^2\text{O} + 3\text{Zn} = 3\text{ZnO} + 3\text{ZnCl}^2 + 2\text{CH}^4$ (Sabanejeff, *Ber.* ix. 1810).

When a mixture of methane and air is passed over a platinum spiral heated to redness by an electric current, the methane is oxidised to formic acid (Coquillion, *Compt. rend.* lxxvii. 444).

Methane, subjected to the influence of the *silent electric discharge*, yields a small quantity of acetylene, together with free hydrogen and resinous hydrocarbons, an odour of turpentine-oil being also evolved (see *ELECTRICITY*, p. 728). Under the same influence, methane combines with *nitrogen*, forming a solid compound (Berthelot, *Compt. rend.* lxxii. 1283).

METHANTHRENE, C₁₅H₁₂ (A. C. Oudemans, *Jour. Deut. Chem. Ges. Ber.* vi. 1125). A hydrocarbon, metameric with methyl-anthracene (p. 94), obtained together with other products, by distilling *podocarpic acid* (q.v.). To separate it, the crude distillate is dissolved in boiling alcohol; the solution is filtered; the mass which separates on cooling is sublimed at 100°–130°; and the sublimate is purified by crystallisation from alcohol and resublimation.

Methanthrene crystallises in white laminae, melts at 117°, boils above 300°, and exhibits a violet fluorescence like that of anthracene. It dissolves easily in boiling, less easily in cold alcohol, very easily in carbon sulphide and glacial acetic acid. When heated it exhales a disagreeable peculiar odour like that of melted asphalt. It forms ill-defined derivatives with bromine and nitric acid; when boiled with potassium dichromate and dilute sulphuric acid, it yields an aromatic acid, probably C₁₅H₁₀O².

Methanthrene-picric acid, C₁₅H₁₂.C₆H₃(NO₂)₃O, is formed by dissolving 4 pts. methanthrene and rather more than 5 pts. picric acid in a small quantity of boiling alcohol, and separates on cooling in very slender orange-coloured needles, which, in the moist state, have the colour of sublimed alizarin, but incline to brown-red when dry. It melts at 117°.

Methanthrene-quinone or *Methanthraquinone*, C₁₅H₁₀O², is formed on adding chromic acid to a warm solution of methanthrene in glacial acetic acid till the liquid assumes a yellow-green colour, and separates on addition of water in yellow-red flocks. By recrystallisation from alcohol and washing with ether, it is obtained in microscopic rhombic laminae. It melts at 187°, distils without alteration at a higher temperature, is insoluble in water, sparingly soluble in ether, freely in alcohol. By an aqueous solution of sulphurous acid, it is converted into hydromethanthrenequinone or methanthrene-quinol.

METHAZONIC ACID, C₂H₃N³O³. The sodium salt of this acid is obtained by acting on nitromethane with alcoholic soda-ley, and heating the resulting crystalline pulp on the water-bath, whereupon it separates into two liquid layers, the upper consisting mainly of alcohol and sodium-compounds soluble therein, the lower of sodium methazonate. The latter may be purified by decanting the upper layer, leaving the remaining liquid to cool, dissolving the crystals which separate in water, and precipitating with alcohol. The sodium salt thus obtained is permanent in the air (unlike sodium-nitromethane), explodes when heated, and forms characteristically coloured precipitates with solutions of the heavy metals, e.g. silver, mercury, copper, and lead (P. Fieser, *Deut. Chem. Ges. Ber.* ix. 324).

According to Locco (*ibid.* 705), the sodium salt and the acid are best prepared by dissolving 4 grams of caustic soda in hot alcohol and adding 5 grams of nitromethane drop by drop. The liquid is then boiled for a short time, and after cooling, the salt which has separated is filtered off, dissolved in water, and decomposed by dilute sulphuric acid. On shaking the liquid with ether, the methazonic acid is dissolved; and the solution is dried over anhydrous sodium sulphate and evaporated over sulphuric acid. A yellow syrup is then left behind, which, on standing, is converted into large crystals, mixed with a thick reddish syrup which colours the skin deep red. For purification, the crystals are pressed between paper and recrystallised from warm benzene.

Methazonic acid is isomeric with ethylnitrolic acid, and is an unstable body, which

1302 METHENYLAMIDOPHENOL—METHYL ALCOHOL.

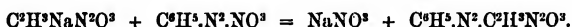
decomposes spontaneously and assumes a red colour. It is readily soluble in water, alcohol, and ether, more sparingly in benzene, and insoluble in petroleum-naphtha. It softens and liquefies at 58°–60°, and explodes at a higher temperature.

The sodium salt crystallises from dilute alcohol in long prisms, and is more explosive than the acid. The methazonates of the heavy metals are obtained by precipitation. The formation of methazonic acid is explained by the equation:



It is perhaps a kind of anhydride of nitromethane; $\left. \begin{array}{l} \text{CH}^2\text{NO} \\ \text{CH}^2\text{NO} \end{array} \right\} \text{O}.$

Azo-compounds of Methazonic Acid (Kimich, *Deut. Chem. Ges. Ber.* x. 140–144). *Azophenyl-methazonic acid*, $\text{C}^6\text{H}^5\text{N}^4\text{O}^2 = \text{C}^6\text{H}^5\cdot\text{N}^2\cdot\text{C}^2\text{H}^2\text{N}^2\text{O}^3$, is precipitated in orange-red flocks on adding a solution of azodibenzene nitrate to an aqueous solution of sodium methazonate. Its formation is expressed by the equation—



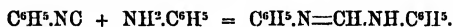
It crystallises from alcohol or ether in fine orange-red needles, which melt with decomposition at 164°. It is nearly insoluble in water, but easily soluble in alcohol, ether, and chloroform. Alkalis dissolve it with deep-red, strong sulphuric acid with yellow colour.

The aqueous solution of the sodium salt, $\text{C}^6\text{H}^5\text{N}^4\text{O}^3\text{Na}^2 + 2\text{H}^2\text{O}$, gives coloured precipitates with copper, cadmium, zinc, mercury, and silver salts. The barium salt, $\text{C}^6\text{H}^5\text{N}^4\text{O}^3\text{Ba} + \text{H}^2\text{O}$, is a purple-red powder.

Azoparatolylmethazonic acid, $\text{CH}^3\cdot\text{C}^2\text{H}^4\cdot\text{N}^2\cdot\text{C}^2\text{H}^2\text{N}^2\text{O}^3$, obtained in the same manner as the preceding compound, forms orange-coloured needles, which melt with decomposition at 154°. It dissolves sparingly in water, very easily in alcohol and ether.

METHENYLAMIDOPHENOL, $\text{C}^6\text{H}^4\langle\text{N}\rangle\text{CH}$, prepared by heating orthamidophenol with formic acid, boils at 182.5°, and after being freed from formic acid by treatment with potassium carbonate, solidifies in transparent shining crystals which melt at 30.5°, and give the vapour-density required by the formula. It is very slowly attacked by air and water. Heated with strong hydrochloric acid, it is decomposed, with formation of orthamidophenol hydrochloride (Ladenburg, *Deut. Chem. Ges. Ber.* x. 1123).

METHENYL-DIPHENYLDIAMINE, $\text{C}^3\text{H}^{12}\text{N}^2 = \text{C}^6\text{H}^5\cdot\text{N}=\text{CH}\cdot\text{NH}\cdot\text{C}^6\text{H}^5$. *Formyl-diphenyldiamine* (W. Weith, *Deut. Chem. Ges. Ber.* ix. 1214).—This base, which Hofmann obtained by the action of chloroform on aniline (iv. 459), is also formed by direct combination when aniline is heated with phenyl cyanide (phenyl-carbamine):



Another mode of producing it is to heat aniline with formic acid in a reflux-apparatus.

Methenyl-diphenyldiamine crystallises in long colourless needles (Hofmann obtained it only as a crystalline powder or in small scales), melts at 135°–136°, and dissolves very easily in alcohol and benzene. The crude product obtained by the action of chloroform on aniline melts at 127°, but when repeatedly crystallised from alcohol and ligroin, it yields needles agreeing exactly with those above described. When methenyl-diphenyldiamine is subjected to prolonged heating in a reflux-apparatus, a small portion of it is resolved into aniline and benzene, but the greater part remains unaltered.

METHIONIC ACID. See METHYLENE-DISULPHONIC ACID, $\text{CH}^2(\text{SO}^2\text{H})^2$ (p. 1313).

METHYL ALCOHOL, $\text{CH}^3\cdot\text{OH}$. *Occurrence.*—This alcohol is almost always found in commercial acetone. Kasantzoff (*Deut. Chem. Ges. Ber.* viii. 436) found it in one sample to the amount of 20 per cent.

Formation.—According to Lieben a. Rossi, and Linnemann a. von Zotta, the distillate obtained by heating calcium formate contains formic aldehyde, which, when treated with sodium-amalgam, yields methyl alcohol (vii. 533). According to Lieben a. Paternò however (*Gazz. chim. ital.* 1873, 290), and Friedel a. Silva (*Compt. rend.* lxxvi. 1545), the distillate in question contains methyl alcohol ready-formed.

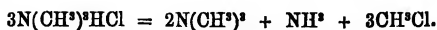
Preparation.—Erlenmeyer finds that the pure methyl oxalate required for the preparation of the alcohol may be very easily obtained by dissolving oxalic acid dehydrated at 100° in boiling methyl alcohol, leaving the solution to cool, draining the

resulting crystals on a vacuum filter, and washing them with cold water, till the liquid which runs through no longer exhibits the iodoform reaction. The ether thus purified is decomposed by prolonged boiling with water (a portion remained unaltered even after three hours' boiling), and the methyl alcohol is distilled off (*N. Rep. Pharm.* xxiii. 624).

Reactions.—Methyl alcohol is oxidised by *electrolytic oxygen*, with evolution of carbon monoxide, together with a small quantity of carbon dioxide, and formation of a liquid containing formate and acetate of methyl (*A. Renard, Compt. rend.* lxxx. 236).

Methyl alcohol, distilled with *sulphuric anhydride* and a large quantity of strong sulphuric acid, is converted into oxymethanesulphonic or methyl-isethionic acid, $\text{CH}(\text{OH})(\text{SO}^3\text{H})^2$ (*q. v.*) (*Max Müller, Ber.* vi. 1031).

METHYL CHLORIDE, CH_3Cl (*C. Vincent, J. Pharm.* [4], xxx. 132). This compound is now prepared in France on a large scale by heating trimethylamine hydrochloride to 260° , whereby it is resolved into ammonia, free trimethylamine and methyl chloride:



By bubbling the vapours through hydrochloric acid, the alkaline gases are retained and the gaseous methyl chloride passes on, to be purified by washing with dilute caustic soda and drying with strong sulphuric acid; it is then collected in a gas-holder, from which it is pumped into strong receivers and liquefied. The tension of its vapour not being high and not increasing very rapidly with the temperature (2.48 atm. at 0° , and 7.50 atm. at 35°), the liquefaction is easily effected, and the transport of the liquid can be carried on without danger.

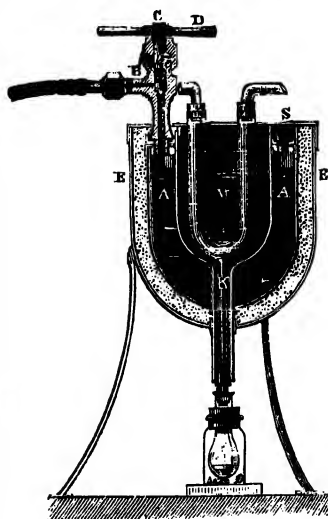
The liquid methyl chloride thus obtained is a most powerful refrigerating agent. When allowed to escape from the receiver into an open vessel, it begins to boil, and in a few moments the temperature of the liquid is lowered by the ebullition below -23° , the boiling-point of the chloride. It then remains for a length of time in a quiescent state, and may be used as a freezing agent. By increasing the rapidity of the evaporation by means of a current of air blown through the liquid, or better by placing the liquid in connection with a good air-pump, its temperature can in a few moments be reduced to -55° , and large masses of mercury easily solidified.

The construction of a small freezing machine employed by M. Vincent is shown in fig. 49. It consists of a double-cased copper vessel, E E, between the two casings of which the methyl chloride A is introduced. The central space M is filled with some liquid such as alcohol, incapable of solidification. The methyl chloride is allowed to enter from the cylindrical reservoir by the screw tap B, and the screw S left open to permit of the escape of the gas. As soon as the whole mass of liquid has been reduced to a temperature of -23° , ebullition ceases, the screw S may be replaced, and if a temperature lower than -23° be required, the tube B placed in connection with a good air-pump. By this simple means a litre of alcohol can be kept for several hours at temperatures either of -23° or -55° , and thus a large number of experiments can be performed, for which hitherto the expensive liquid nitrous oxide or solid carbonic acid was required.

M. Vincent has recently constructed a much larger and more perfect and continuous form of freezing machine, in which by means of an air-pump and a forcing-pump the chloride of methyl is evaporated in the freezing machine and again condensed in the cylinders. This enlarged form of apparatus will probably be found more convenient and economical than the ether and sulphurous acid freezing machines now in use, as it can be simply constructed, the vapour and liquid do not attack metal and are not poisonous, and the frigorific effects produced are extremely energetic.

Another and perhaps more important application of methyl chloride is to the manufacture of the blue, green, and violet dyes produced by replacing part of the

FIG. 49.



hydrogen in rosaniline by methyl. This substitution has hitherto been effected chiefly by the use of the expensive iodide of methyl: the chloride will afford a much more economical method of obtaining them (see ROSANILINE).

The trimethylamine from which the methyl chloride is prepared in the manner above described, is obtained from the spent liquors (*vinasses*) of the stills in which the molasses of beet-juice are distilled for the production of alcohol (see METHYLAMINES).

METHYL OXIDE, $(\text{CH}_3)_2\text{O}$, is formed, together with the chlorides of tri- and tetra-methylammonium, by heating sal-ammoniac with excess of methyl alcohol (Weith, *Deut. Chem. Ges. Ber.* viii. 458).

Preparation.—Erlenmeyer a. Kriechhauer (*Ber.* vii. 699) prepare this compound by gradually heating 13 pts. methyl alcohol and 20 pts. sulphuric acid to 140° in a reflux apparatus, washing the evolved gas with soda-ley, and passing it into sulphuric acid, which absorbs 600 vols. of it, forming the compound $\text{SO}(\text{OH})\cdot(\text{OCH}_3)_2$, which may be kept without alteration, and gives off methyl oxide when 1 pt. of it is added by drop to 1 pt. of water.

For preparation on the large scale, a mixture (34°Bm.) of 1 pt. sulphuric acid and rather more than 1 pt. anhydrous wood-spirit is heated to 125° – 128° , as long as methyl oxide continues to be evolved, care being taken that the temperature does not rise above 130° ; it is then left to cool, and to the remaining liquid, marking 45°Bm. , more wood-spirit is added sufficient to lower the density to 34°Bm. ; and by thus alternately heating, cooling, adding fresh wood-spirit, and again heating, &c., as in the preparation of ethyl oxide, large quantities of methyl alcohol may be etherified with only a small quantity of acid. The methyl ether, which is given off as vapour, is freed from carbon dioxide and sulphur dioxide by means of caustic potash, caustic soda, or sugar-lime, and from water by calcium chloride, and finally condensed (Tollier, *Arch. Pharm.* [3], x. 57).

On the Friction-coefficient of Methyl-oxide, see GASES (p. 851 of this volume). On its Imperfect Combustion, p. 436.

METHYL SELENIDE or **SELENMETHYL**, $(\text{CH}_3)_2\text{Se}$ (C. I. Jackson, *Liebig's Annalen*, cxxix. 1). To prepare this compound, phosphorus pentaselenide (obtained by heating an intimate mixture of 5 at. selenium with rather more than 2 at. phosphorus) is coarsely pulverised and drenched in a retort with a mixture of strong soda-ley and a solution of potassium methyl-sulphate. On gently heating the mixture, it froths up, and yields a distillate of water and a yellow liquid, which may be separated from the water by a tap-funnel, and purified by fractional distillation; it then yields, as chief product, methyl monoselenide. If a stronger heat be employed in the preparation, a few drops of a yellow, less volatile liquid pass over, probably consisting of the diselenide, $(\text{CH}_3)_2\text{Se}_2$, and identical with the product which Wöhler a. Dean obtained by distilling barium methylsulphate with potassium selenide (iii. 990).

Methyl monoselenide is a colourless, strongly refracting liquid, having a very offensive odour and boiling at 32° . It sinks in water; is decomposed, with separation of selenium, when boiled therewith, and mixes with alcohol and ether. It unites with acid radicles, forming a series of compounds analogous to those of benzyl selenide (p. 316).

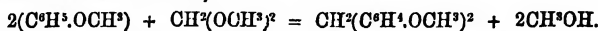
Selenmethyl Nitrate, either $(\text{CH}_3)_2\text{Se}(\text{NO}_3)_2$, $(\text{CH}_3)_2\text{SeO}$ or $(\text{CH}_3)_2\text{Se} \begin{smallmatrix} \text{NO}_3 \\ \text{OH} \end{smallmatrix}$, is formed by adding selenmethyl to strong nitric acid in a vessel which is kept cool, and crystallises, on evaporating the solution over the water-bath, in long colourless prisms. It melts at 90.5° , volatilises below 100° , dissolves easily in water, sparingly in alcohol, and is insoluble in ether. The *dichloride*, $(\text{CH}_3)_2\text{SeCl}_2$, precipitated from a strong solution of the nitrate by hydrochloric acid, forms white nacreous laminæ, melting at 59.5° , very soluble in alcohol, less soluble in ether, sparingly in water. The *dibromide*, $(\text{CH}_3)_2\text{SeBr}_2$ prepared in like manner with hydrobromic acid, and purified by washing the precipitate with cold water, and once crystallising it from alcohol, forms broad sulphur-yellow nacreous laminæ having a very unpleasant odour. It melts and decomposes at 82° , and is partially decomposed by boiling with alcohol, in which it is but slightly soluble; it is also sparingly soluble in water, and insoluble in ether. The same compound is formed directly by direct combination of selenmethyl with bromine. The *di-iodide*, precipitated from the nitrate by potassium iodide, is a brick-red, easily decomposable powder, insoluble in water, easily soluble in alcohol and in ether. The *platinochloride*, $[(\text{CH}_3)_2\text{Se}]^2\text{PtCl}_4$, obtained by mixing the monoselenide with solution of platinic chloride, and boiling the resulting pale-red precipitate with water, crystallises in lemon-yellow laminæ, nearly insoluble in water, quite insoluble in ether, sparingly soluble in hot alcohol. When heated, it blackens and gives off methyl monoselenide.

METHYL SULPHIDE, $(\text{CH}_3)_2\text{S}$. On the reaction of this compound with benzyl sulphide and methylene sulphide, see SULPHINES. On its reaction with *brom-acetic acid*, see METHYL-THIETINE (p. 1317).

METHYLACETANILIDE, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)(\text{C}^2\text{H}_3\text{O})$. See METHYLANILINES (p. 1306) and BENZENES (METHYLAMIDO-), p. 204 of this volume.

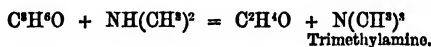
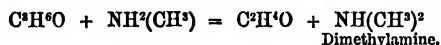
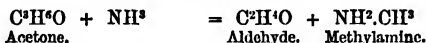
METHYL-ACETOSUCCINIC ETHERS. See SUCCINIC ETHERS.

METHYLAL, $\text{C}^2\text{H}^2\text{O}^2 = \text{CH}^2(\text{OCH}^3)^2$. This compound is related to form-aldehyde, CH^2O , in the same manner as acetal, $\text{C}^2\text{H}^4(\text{OC}^2\text{H}^3)^2$, to acetaldehyde, $\text{C}^2\text{H}^4\text{O}$. When mixed with anisole, in presence of glacial acetic acid, the vessel being kept cool, it forms dimethoxyphenyl methane (p. 649), and methyl alcohol (ter Meer, *Deut. Chem. Ges. Ber.* vii. 1200):



METHYL-ALIZARIN, $\text{C}^{18}\text{H}^{10}\text{O}^4$. See METHYL-ANTHRAQUINONE.

METHYLAMINES. *Mono*-, *di*-, and *tri*-methylamine are found in commercial wood-spirit; and their occurrence, together with aldehyde, may be attributed to the mutual action of ammonia and acetone, which are also constituents of the crude product of the distillation of wood. The reactions may be represented by the following equations:



(C. W. Vincent, *Compt. rend.* lxxvii. 898; *Ann. Chim. Phys.* [5], i. 444). The formation of methylamine and aldehyde by the above reaction has been experimentally demonstrated by Camille.

Methylamine is also formed: *a*. By the reduction of nitromethane with iron filings, acetic acid, and water (Preibisch, *J. pr. Chem.* [2], vii. 480). *β*. Together with triethylamine hydrochloride, tetrethylammonium chloride, and methylic ether, by heating sul-ammoniac (12 grams) with methyl alcohol (12 c.c.) for six hours to 280°–285° (Weith, *Ber.* viii. 458). *γ*. Together with glycocine, ammonia, and carbon dioxide, by heating methyluric acid to 170° with hydrochloric acid saturated at 0° (H. Hill, *Sill. Am. J.* [3], xii. 428).

The base called *mercurialine*, from *Mercurialis perennis*, is identical with methylamine (E. Schmidt, *Ber.* x. 2226).

Trimethylamine, $\text{N}(\text{CH}_3)^3$.—This base is now obtained in large quantities from the waste-liquors or spent wash (*vinasses*) of the stills in which the molasses of beet-root sugar is distilled for the production of alcohol. It has long been the custom in France to evaporate those liquors to dryness, and calcine the mass in a reverberatory furnace, with the view of recovering the alkaline salts of the beet root, to be used as manure. By this treatment, the volatile organic products, viz. the ammonia-water, tar, and oils, were of course destroyed; but recently M. Camille Vincent of Paris has succeeded in collecting these products and turning them to profitable account.

The following is an outline of the process, as carried out at the large distillery of Messrs. Tilloy, Delaune, and Co., of Courrières. The spent-wash, having been evaporated until it has attained a sp. gr. of 1.31, is allowed to run into cast-iron retorts, in which it is submitted to dry distillation. This process lasts four hours; the volatile products pass over, whilst a residue of porous charcoal and alkaline salts remains behind in the retort. The gaseous products given off during the distillation are passed through coolers, in order to condense all the portions which are liquid or solid at the ordinary temperature, and the combustible gases pass on uncondensed and serve as fuel for heating the retorts.

The liquid portion of the distillate is a very complex mixture of chemical compounds, resembling in this respect the corresponding product in the manufacture of coal-gas. Like this latter, the liquid distillate from the spent-wash may be divided into ammonia-water and tar. The ammonia-water of the vinasse resembles that of the coal-gas manufacture in so far as it contains carbonate, hydrosulphide, and hydrocyanide of ammonia; but it differs from this (and approximates to the products of the dry distillation of wood) by containing in addition methyl alcohol, methyl sulphide, methyl cyanide, many of the members of the fatty acid series, and large quantities of the salts of trimethylamine. The tar, on re-distillation, yields more ammonia-

water, a large number of oils, the alkaloïds of the pyridine series, solid hydrocarbons, carbolic acid, and, lastly, a pitch of fine quality.

The crude alkaline aqueous distillate is first neutralised by sulphuric acid, and the saline solution evaporated, when crystals of sulphate of ammonia are deposited; and these, after separating and draining off, leave a mother-liquor, which contains the more soluble sulphate of trimethylamine. During the process of concentration, vapours of methyl alcohol, methyl cyanide, and other nitrils are given off, these being condensed, and the cyanide used for the preparation of ammonia and acetic acid by decomposing it with alkali.

Trimethylamine itself has not yet been applied to any industrial use; but its hydrochloride, when heated to 260° , is resolved, as already explained (p. 1303), into trimethylamine, ammonia and methyl chloride, which may be utilised as a refrigerating agent, and, instead of the iodide, for the preparation of methylated anilino dyes (C. Vincent, *Compt. rend.* lxxxiv. 1139; lxxxv. 667; *J. Pharm.* [4], xxx. 132). See also a lecture by Professor Roscoe 'On a New Chemical Industry' (*Chem. News*, xxxix. 107).

A mixture of trimethylamine and aniline hydrochloride yields, when heated, a distillate of methylaniline.

Trimethylamine hydrobromide is resolved between 230° and 300° into trimethylamine, ammonia, and methyl bromide. Trimethylamine hydriodide crystallises in white shining tables, which gradually turn brown on exposure to the air, and at about 210° begin to decompose, with evolution of white vapours, into trimethylamine, ammonia and methyl iodide, tetramethylammonium iodide being also formed by a secondary reaction (Vincent, *loc. cit.*)

Trimethylamine is one of the basic constituents of the aqueous extract of hops (Griessmayer, p. 1040).

Tetramethylammonium Ferrocyanide, $\text{FeCy}^2[(\text{CH}_3)_4\text{NCy}]^4$, is formed by the action of hydroferrocyanic acid on tetramethylammonium hydroxide, the two substances being mixed in aqueous solution, and the product evaporated in a vacuum over sulphuric acid. The compound crystallises in lamino-granular masses containing, when air-dried, 13 mol. H_2O , which, by successive drying over calcium chloride and sulphuric acid, and heating to 100° – 140° , may be reduced to 2 mol., the remainder being given off, with decomposition, at a temperature above 140° . The salt has not yet been obtained pure and anhydrous (L. Barth, *Ber.* viii. 1484).

Tetramethylammonium Iodide is perfectly stable at high temperatures (Hofmann, *Deut. Chem. Ges. Ber.* vii. 526).

METHYL-AMYL, $\text{C}^6\text{H}^{11} = \text{CH}^3.\text{C}^5\text{H}^{11}$, is formed together with diamyl and ethane, by the action of sodium on a mixture of methyl iodide and optically active amyl iodide. It is a liquid boiling at 60° (Le Bel, *Bull. Soc. Chim.* [2], xxv. 546).

METHYLANILINES. *Monomethylaniline*, $\text{C}^6\text{H}^5\text{N} = \text{C}^6\text{H}^5.\text{NH}(\text{CH}_3)$.—The formation of this base, by the action of methyl bromide or iodide on aniline, as discovered by Hofmann in 1850 (iv. 453), has lately been called in question by A. Kern (*Deut. Chem. Ges. Ber.* 1877, 195), who regards the product thus obtained as a mixture of aniline and dimethylaniline. Hofmann, however (*ibid.* 591), by renewed experiments, has confirmed the correctness of his former conclusions, and has shown that monomethylaniline is produced, together with dimethylaniline, by the action of the chloride, as well as of the bromide or iodide of methyl, on aniline. *Chloride of methyl* acts on aniline at the boiling heat, the liquid product on cooling depositing crystals of aniline hydrochloride; on adding anhydrous ether and treating the resulting solution with dilute sulphuric acid, an additional quantity of aniline is separated as sulphate, and the remaining ethereal solution leaves, on evaporation, a basic oil consisting of a mixture of mono- and dimethylaniline, separable by means of acetic anhydride, which converts the monomethylaniline, with great rise of temperature, into methylacetanilide, while the dimethylaniline remains unaltered. The methylacetanilide, distilled with an alkali, yields methylaniline. *Bromide and iodide of methyl* act on aniline dissolved in ether at ordinary temperatures, the solution in the first case depositing aniline hydrobromide in the course of twenty-four hours, and in the second, aniline hydriodide after some days. The remaining ethereal solution contains mono- and dimethylaniline, which may be separated as above by means of acetic anhydride.

In all cases, the largest yield of monomethylaniline is obtained when a considerable excess of aniline is used, the amounts in Hofmann's experiments being, with methyl iodide, 21.2 per cent., with methyl bromide 25.2 per cent., and with methyl chloride 45.7 per cent. of the aniline attacked. The reaction, however, takes place in the same manner with smaller proportions of aniline; thus, 1 mol. methyl iodide and

1 mol. aniline yielded, after prolonged action and repeated distillation, a quantity of monomethylaniline equal to 12·5 per cent. of the aniline attacked, the remainder being converted into dimethylaniline. A mixture of 40 pts. aniline hydrochloride, 60 aniline and 35 methyl alcohol, yielded, on the manufacturing scale, a product consisting of 25 aniline, 30 mono-, and 45 dimethylaniline.

Commercial methylaniline is almost always contaminated with aniline and dimethylaniline. The aniline may be removed by adding dilute sulphuric acid, and separating the resulting crystals of aniline sulphate from time to time by pressing the liquid (undissolved base and sulphate solution) through linen, the addition of sulphuric acid being discontinued when the filtrate after this treatment no longer yields any crystals. The mono- and dimethylated bases (retaining only traces of aniline), after being set free by an alkali, may then be separated by acetyl chloride, which, like the corresponding anhydride, acts only on the monomethylated base. As the action is very violent, it is best to add the chloride through a tap-funnel to the mixture of bases contained in a reflux apparatus. On subsequently shaking out the product into hot water, it dissolves, and the solution on cooling deposits methylacetanilide in large crystals, which may be easily and completely purified by recrystallisation. It melts at 99·5°, and distils, without alteration, at 245°. The separation of methylaniline from this compound is best effected by boiling hydrochloric acid.

Pure monomethylaniline has a density of 0·276 at 15°, and boils at 190°–191° (pure dimethylaniline at 191°–192°). It forms a beautiful platinochloride, and gives no colour reaction with solutions of chloride of lime. Its oxalate, when heated, does not yield aniline (Hofmann, *Deut. Chem. Ges. Ber.* vii. 523; x. 591).

Ch. Girard (*Bull. Soc. Chim.* [2], xxiv. 120) prepares mono- and dimethylaniline by heating methyl alcohol with aniline and hydrochloric acid at 190°–200° under pressure. Noetting a. Boasson (*ibid.* xxviii. 2) have prepared monomethylaniline in large quantity by this process, and by the action of methyl iodide on aniline, and separate it from aniline and dimethylaniline by treatment with nitrous acid, whereby the last two are converted respectively into diazobenzene nitrate and nitroso-dimethylaniline, $C^6H^4(NO)N$, both of which are soluble in water, whilst the monomethylaniline

yields methylphenylnitrosamine, $\begin{matrix} CH^3 \\ C^6H^5 \end{matrix} > N-NO$, in the form of a yellow oil insoluble in water and in acids, and converted by reduction into monomethylaniline. The reaction may be applied to the estimation of monomethylaniline. The substance under examination, having been treated with nitrous acid, is exhausted with ether, which dissolves the methylphenylnitrosamine; the extract is then dried; the ether is evaporated; and the methylphenylnitrosamine, which remains in the form of an oil, is weighed. Dimethylaniline, similarly treated, yields a few yellow crystals but no oil.

Dimethylaniline, $C^6H^{11}N = C^6H^5.N(CH^3)^2$. On the formation of this base, see page 1305. *Reactions.* 1. *Decomposition by Heat.*—When the vapour of dimethylaniline is passed through a combustion-tube filled with fragments of glass and heated to low redness, benzonitril is obtained as chief product (25 per cent. of the dimethylaniline decomposed), together with imido-diphenyl, $NH(C^6H^5)^2$ (the so-called carbazol, vii. 253), and a small quantity of benzene, besides ammonia and hydrogen cyanide (Nietzki, *Deut. Chem. Ges. Ber.* x. 474).

2. With *Sulphur Chloride*, S^2Cl^2 , dimethylaniline forms dithiodimethylaniline, $[C^6H^4N(CH^3)^2]^2S^2$, an easily crystallisable, nearly indifferent compound (Hannimann, *Ber.* x. 403).

3. With *Sulphuryl Chloride*, SO^2Cl^2 , the product formed is dimethyldichloraniline, $C^6H^4Cl^2.N(CH^3)^2$, which crystallises slowly from aqueous solution in needles (Wenghöffer, *J. pr. Chem.* [2], xvi. 448). *Ethylsulphuric chloride*, $SO^2Cl(OC^2H^5)$, acts violently on dimethylaniline, converting it into dimethylparamidobenzene-sulphonic or dimethylsulphanilic acid, $(CH^3)^2N.C^6H^4.SO^3H$ (Wenghöffer).

4. Dimethylaniline is converted by *perchloromethane* at 180° into carbotetradi-methylaniline, $C[C^6H^4N(CH^3)^2]^4$, and by *chloroform* at 230° into methenyltri-dimethylaniline, $CH[C^6H^4N(CH^3)^2]^3$. Both these compounds are basic, crystallise in laminæ, melt at 81°–83°, and resemble each other in their behaviour with various reagents. Heated with dilute sulphuric acid, the first yields CO , the second CO^2 . The same products are formed, together with methyl chloride and aniline hydrochloride, when these compounds are heated to 220° with strong hydrochloric acid (Hannimann, *Deut. Chem. Ges. Ber.* x. 1689).

5. When dimethylaniline (3 mol.) is heated with *benzyl chloride* (2 mol.) and *bromine* (2 mol.) to 120° in a reflux apparatus for four hours, a sea-green body is obtained, which is insoluble in water, dissolves with blue colour in alcohol, and dyes silk blue-green. With a smaller proportion of benzyl chloride, blue dye-stuffs are produced (Brunner a. Brandenburg, *Ber.* x. 1844).

6. When to a cooled mixture of *benzaldehyde* (20–30 grams), with four or five times that quantity of dimethylaniline—the excess of which acts as a diluent—zinc chloride is gradually added till a thick paste is formed, an equal volume of water added after about an hour, the whole boiled in a reflux apparatus, and the product made alkaline with caustic soda and largely diluted with water, ether will extract from it—together with unaltered materials which may be removed by distillation with steam—a base, $C^{23}H^{26}N^2 (= 2C^6H^{11}N + C^7H^{10}O - H^2O)$, which may be purified by repeated crystallisation from a moderate quantity of alcohol, and separates therefrom in white roundish crystals, appearing, when examined by a lens, as groups of small concentrically arranged needles. This base melts at 92° – 93° ; dissolves readily in ether, and with moderate facility in alcohol; retains its pure white aspect when kept in the dry state in closed vessels; but assumes a faint blue-green colour on exposure to the air. The *picrate*, $C^{23}H^{26}N^2 \cdot 2C^6H^2(NO^2)_3OH$, is obtained by adding picric acid to an ethereal solution of the base, as a yellow precipitate, which dissolves with yellow-green colour in alcohol, and crystallises therefrom in small yellow needles. The *platinochloride*, $C^{23}H^{26}N^2 \cdot 2HCl.PtCl_4$, obtained by adding an ethereal or alcoholic solution of the base to an acid solution of platinic chloride, is a white precipitate which assumes a dingy green colour on exposure to the air. The other salts, especially the sulphate, nitrate, and hydrochloride, quickly oxidise, especially in alcoholic solution, to dye-stuffs of fine blue-green colour, and often of complex constitution (O. Fischer, *Ber.* x. 1624).

7. A mixture of dimethylaniline and *furfural*, treated as above with zinc chloride, yields a base which separates from alcoholic solution in fine crystals usually somewhat coloured, but becoming quite white after repeated crystallisation from ligroin. This base melts at about 70° . Its salts exhibit a tendency to oxidise to red dye-stuffs. From the analysis of the platinochloride, it appears to have the composition $C^{23}H^{24}N^2O = 2C^6H^{11}N + C^5H^4O^2 - H^2O$ (Fischer, *ibid.* 1626).

Bromodimethylaniline, $C^{11}H_7Br.N(CH^3)_2$, is formed on gradually adding bromine to a solution of dimethylaniline in 5 pts. of glacial acetic acid. It is precipitated by soda-ley from the dilute solution as a grey crystalline powder, which is most readily purified by solution in hydrochloric acid and precipitation with caustic soda. It crystallises from alcohol in silvery laminae, volatilises with vapour of water, melts at 55° , and boils at 247° (bar. 722 mm.) Its salts are very soluble and deliquescent. The *hydrochloride*, obtained by passing hydrogen chloride into a solution of the base in benzene, very easily parts with its acid, and is completely soluble only in acidulated water. The *platinochloride* is granulo-crystalline.

Bromodimethylaniline is not attacked by strong soda-ley or hydrochloric acid at the boiling heat; but at 180° – 200° it is resolved by hydrochloric acid into methyl chloride and monobromaniline, melting at 16° , a small quantity of bromophenol being probably formed at the same time (A. Weber, *Ber.* x. 760).

Brunner a. Brandenburg (*ibid.* 1844), by acting on dimethylaniline with bromine in the manner described by Weber, obtained, instead of the compound just described, a blue-violet colouring matter having the composition of tetramethyl-rosaniline hydrobromide, $C^{20}H^{18}(CH^3)_4N^2 \cdot 4HBr$, which they find is also produced by the action of bromine on dimethylaniline without the intervention of a solvent. Probably bromodimethylaniline was the first product of the reaction, and was subsequently converted into tetramethyl-rosaniline (see ROSANILINE).

Iododimethylaniline, $C^8H^7I.N(CH^3)_2$, is formed: α . By the action of *iodine* on dimethylaniline, both being dissolved in carbon disulphide (Weber, *loc. cit.*) β . By the action of *cyanogen iodide* on dimethylaniline, which takes place in the cold, and is attended with rise of temperature and evolution of hydrogen cyanide.

Iododimethylaniline crystallises in white laminae, melts at 79° , and dissolves in alcohol and hydrochloric acid. Its *platinochloride* crystallises well. The base is not attacked by caustic soda. It turns bluish at ordinary temperatures, and decomposes when heated above its melting point, with rapid evolution of hydrogen iodide, leaving a dark-coloured mass, which dissolves in alcohol with deep violet colour (Weber).

Nitrodimethylanilines. *Paranitrodimethylaniline*, $C^8H^4(NO^2).N(CH^3)_2$, is formed by gradually adding the calculated quantity of nitric acid to a solution of dimethylaniline in 10 to 12 pts. of glacial acetic acid. A rapid action then takes place, the liquid on cooling, and further on addition of water, depositing yellow needles; and on recrystallising these several times from alcohol, the nitrodimethylaniline is obtained—together with a cinnabar-red substance less soluble in alcohol, more soluble in benzene than itself—in yellow needles having a steel-blue lustre and melting at 163° . Nitrodimethylaniline does not form salts, and is not altered by boiling with hydrochloric acid, in which it dissolves, or with soda-ley. By hydro-

chloric acid at 180° – 200° it is decomposed into methyl chloride and other bodies (A. Wober, *Ber.* x. 760). The same nitrodimethylaniline was previously obtained by Schraube (*Ber.* viii. 616), by oxidising nitrosodimethylaniline with potassium ferricyanide, or better with permanganate. Schraube described this product as melting at 167° , and as possessing basic properties; but Wurster (*Ber.* xii. 528) has shown that it is identical with the nitrodimethylaniline obtained by Weber, both products melting at 162° , being destitute of basic properties, and convertible by reduction with tin and hydrochloric acid into dimethyl-paraphenylenediamine.

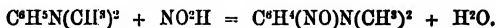
Paramidodimethylaniline.—The stannosochloride of this base,



produced by treating paranitrodimethylaniline with tin and hydrochloric acid, crystallises from alcohol in cubes. The free base boils almost without decomposition; when exposed to the air it becomes brown and viscid. The *hydrochloride*, treated with weak oxidising agents, very quickly acquires a deep red to violet colour; the same change is produced in it by platonic chloride. At 180° it is resolved by dry hydrogen chloride into methyl chloride and paraphenylenediamine; by oxidation, into quinone (Weber).

Dinitrodimethylaniline is obtained by oxidising nitrosodimethylaniline with dilute nitric acid, and forms large sulphur-yellow crystals melting at $73\cdot5^{\circ}$ (Schraube). Weber, by the action of nitric acid on dimethylaniline dissolved in 6 or 7 pts. of glacial acetic acid, obtained it in needles melting at 77° .

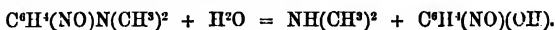
Nitrosodimethylaniline, $\text{C}^6\text{H}^4(\text{NO})\text{N}(\text{CH}^3)_2$ (Baeyer u. Caro, *Deut. Chem. Ges.* *Ber.* vii. 809, 963; Schraube, *ibid.* viii. 61). This base is formed by the action of nitrous acid on dimethylaniline:



Baeyer u. Caro prepare it by adding 100 pts. of amyl-nitrite to a mixture of 50 pts. of dimethylaniline, 100 pts. of concentrated hydrochloric acid, and 750 pts. of a mixture of 1 vol. of hydrochloric acid with 2 vol. of alcohol, well cooled with ice. After a short time, yellow needles separate; as soon as these no longer increase in quantity, the mass is thrown on a vacuum-filter and washed with ether-alcohol. An almost quantitative yield of pure nitrosodimethylaniline hydrochloride is thus obtained, in the form of small sulphur-yellow needles. Schraube adds 75 pts. amyl nitrite cooled to 0° to an ice-cold mixture of 50 pts. dimethylaniline, 100 pts. strong hydrochloric acid, and 600 pts. alcoholic hydrochloric acid (1 vol. acid to 2 vol. alcohol).

The crystals of the hydrochloride melt at 177° , but are apparently decomposed at the same time; they dissolve in water, forming a deep yellow solution, and on adding potassium carbonate to this solution, the pure base separates in green flakes; it may be dissolved out by ether, and separates from the solution on evaporation in large green plates which melt at 92° (Baeyer u. Caro), at 85° (Schraube), and are slightly volatile in a current of steam. The salts crystallise well. The *sulphate* and *nitrate* are obtained in slender yellow needles on adding sulphuric or nitric acid to an ethereal solution of the base (Baeyer u. Caro). The *oxalate* crystallises from wood-spirit in brown-red monoclinic crystals containing 2 mol. water (Schraube).

Nitrosodimethylaniline is oxidised by *ferricyanide* or *permanganate of potassium* to nitrodimethylaniline. By boiling with *alkalis*, it is resolved into dimethylaniline and nitrosophenol (Baeyer u. Caro):



By *tin* and *hydrochloric acid*, it is reduced to dimethylphenylenediamine, a very unstable base, the nitrate and sulphate of which crystallise at first in colourless needles, but are very easily decomposed (Schraube).

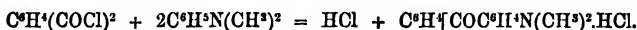
Nitrosodimethylaniline hydrochloride is converted by *alcoholic potash* into tetramethyldiamidazoxybenzene, which crystallises in brown shining needles, very sparingly soluble in water, wood-spirit, ether, acetic acid, and ligroin, easily in chloroform. This compound is not reduced by alcoholic ammonium sulphide, sulphurous acid, or sodium-amalgam, but by tin and hydrochloric acid it is easily reduced to dimethylphenylenediamine. Its *salts* form brownish-yellow laminae, which are completely decomposed by water. Its *platinochloride* is very slightly soluble, and gives a variable amount of platinum (Schraube).

Addition-products, in the form of large splendid dark steel-blue crystals, are obtained by heating a solution of nitrosodimethylaniline in alcohol or benzene with *aniline* or *paratoluidine*. The compound of nitrosodimethylaniline with *dimethylaniline* crystallises from benzene in dark green shining crystals, which quickly effloresce

on exposure to the air. The *phenol-compound*, $2\text{C}^6\text{H}^4(\text{NO})\text{N}(\text{CH}^3)_2 \cdot \text{C}^6\text{H}^5\text{O}$, formed by mixing the components in the required proportions, with addition of water, crystallises in brown slender needles, which give off all their phenol at 70° . Nitrosodimethylaniline also combines with *silver nitrate*, forming a compound which crystallises from water at 25° in small shining crystals, dark blue by reflected, violet by transmitted light (Schraube).

Benzoyl-dimethylaniline, $\text{C}^6\text{H}^5 \cdot \text{CO} \cdot \text{C}^6\text{H}^4 \cdot \text{N}(\text{CH}^3)_2$, is formed (by heating dimethylaniline with *benzoic acid* and *phosphoric anhydride* to 180° – 200° in a sealed tube for six to eight hours. On exhausting the product with ether, agitating the ethereal solution with potash-ley and hydrochloric acid, and leaving it to evaporate, benzoyl-dimethylaniline remains in the form of an oil which boils at 330° – 335° . It dissolves in petroleum-ether, and crystallises therefrom in rosettes of white needles; dissolves also in the ordinary solvents. With *fuming nitric acid* it forms a dinitro-derivative which dissolves readily in glacial acetic acid, crystallises in nodules, and melts at 142° ; and with *bromine*, a derivative crystallising in needles (O. Fischer, *Ber.* x. 953).

Dimethylaniline-phthalein, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 = \text{C}^6\text{H}^4[\text{COC}^6\text{H}^4\text{N}(\text{CH}^3)_2]^2$ (O. Fischer, *Ber.* ix. 753; x. 952). This compound is formed, as a hydrochloride, by the action of phthalic chloride on dimethylaniline:



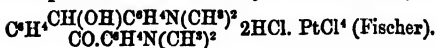
The two bodies, on mixing, become hot, and the mixture acquires a dark brown colour. On heating it for a short time, the colour changes to yellowish green, a violent frothing takes place, and the thickened mass becomes dark green. The reaction is facilitated by small quantities of zinc-dust. As soon as the frothing is over, water is added to prevent further decomposition, and the excess of dimethylaniline is driven off with the steam. The residue solidifies on cooling to a resin having a roddish surface-shimmer, and may be ground to a deep green powder. The crude product, which dissolves easily and with green colour in alcohol, wood-spirit, chloroform, and acetic acid, sparingly in water, and scarcely at all in ether, is purified by repeatedly boiling it with ether, dissolving it in a small quantity of alcohol, mixing the solution with water, and crystallising the resulting precipitate from chloroform.

Dimethylaniline-phthalein is also formed by the action of dehydrating agents, (ZnCl^2 , P^2O^3), on a mixture of phthalic anhydride and dimethylaniline. It separates from the solution of the hydrochloride, on addition of alkalis, in greenish-white granules which become colourless when freed from the liquid by filtration, but turn green again on drying. It dissolves in alcohol, ether, and wood-spirit, and crystallises from the last in granular masses. It is scarcely attacked by potassium hydroxide at 200° , but is resolved thereby at higher temperatures into phthalic acid and dimethylaniline. Phthalic acid is also formed when a mixture of the phthalein with strong nitric acid is evaporated down on the water-bath.

The *monohydrochloride*, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot \text{HCl}$, prepared as above described, crystallises in small needles having a greenish-yellow lustre. The *dihydrochloride*, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot 2\text{HCl}$, is obtained on adding dry hydrochloric acid to the ethereal solution of the base, previously dried by calcium chloride, as a yellow-red, crystalline, extremely hygroscopic precipitate, which, when heated in the water-bath, gives off hydrogen chloride and is converted into the green salt.

Platinochlorides.—($\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot \text{HCl}$) $^2\text{PtCl}^4$, is obtained as a blue-green crystalline precipitate on adding an alcoholic solution of platonic chloride to an alcoholic solution of the monohydrochloride; it is very easily soluble in water. Another salt, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot 2\text{HCl} \cdot \text{PtCl}^4$, is obtained by adding a solution of the base in strong hydrochloric acid to alcoholic platonic chloride, as a yellowish-red crystalline precipitate, easily soluble in water, sparingly in alcohol and ether. The *picrate*, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot \text{C}^6\text{H}^2(\text{NO}^2)_3\text{OH}$, prepared by adding an alcoholic solution of picric acid to an alcoholic solution of the monohydrochloride, is a dark green precipitate. A yellow picrate, $\text{C}^{24}\text{H}^{24}\text{N}^2\text{O}^2 \cdot 2\text{C}^6\text{H}^2(\text{NO}^2)_3\text{OH}$, is precipitated on adding a solution of the dihydrochloride to aqueous picric acid. The other salts of dimethylaniline-phthalein crystallise well.

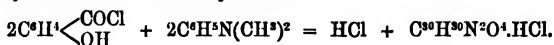
Base obtained by reduction of Dimethylaniline-phthalein.—When an acid solution of the phthalein is reduced with zinc-dust, it becomes decolorised, and soda-ley added to the solution throws down a colourless base, the colourless salts of which easily turn green by oxidation. The *picrate* has a light yellow colour, and the *hydrochloride* gives with *platinic chloride* a nearly colourless precipitate, probably having the composition



Bromodimethylaniline-phthaleïn, $C^{21}H^{22}Br^2N^2O^2$.—The *monohydrochloride* of this base, formed by heating bromodimethylaniline (p. 130) with phthalic chloride, crystallises from alcohol in feathery groups of steel-blue needles, easily soluble in alcohol, wood-spirit, chloroform, and glacial acetic acid, sparingly in water. From its solution in strong hydrochloric acid, water throws down the dingy green *dihydrochloride*, $C^{21}H^{22}Br^2N^2O^2 \cdot 2HCl$. The alcoholic solution of the monohydrochloride is blue-violet; its solution in wood-spirit has a violet colour more inclining to red; the chloroform solution is almost pure blue. The *platinochloride*, $2(C^{21}H^{22}Br^2N^2O^2 \cdot HCl) + PtCl_4$, is a blue crystalline powder. The free base has a blue-violet colour, dissolves in alcohol and ether, and yields a green *picrate* (O. Fischer, *Ber.* x. 1623).

Hexnitrodimethylaniline-phthaleïn, $C^{21}H^{18}N^6O^{14}$, is formed by digesting the hydrochloride of the phthaleïn with fuming nitric acid on the water-bath, and separates, on pouring the resulting liquid into water, in flocks, which are best recrystallised from glacial acetic acid. It dissolves easily in acetone, less easily in alcohol, ether, wood-spirit, and chloroform, not at all in water, easily and with red-brown colour in nitric and sulphuric acids. From glacial acetic acid it separates in small yellow crystals, which melt at 190° – 193° , and detonate when quickly heated (O. Fischer, *Ber.* x. 952).

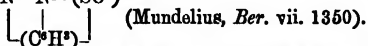
Dimethylaniline-saliceïn, $C^{30}H^{30}N^2O^4$, is formed, as a hydrochloride, by heating salicyl chloride with dimethylaniline:



The reaction, which is attended with evolution of hydrogen chloride, is facilitated by the addition of very small quantities of zinc-dust.

The *hydrochloride*, $C^{30}H^{30}N^2O^4 \cdot HCl \cdot 2H^2O$ (after drying at 100°), may be obtained, as a flocculent precipitate, by washing with water, solution in hydrochloric acid, precipitation by large addition of water, and finally solution in chloroform and precipitation with ether. It dyes silk much like methyl-green, and is of much higher tinctorial power than dimethylaniline-phthaleïn. It forms two *platinum-salts*, $C^{30}H^{30}N^2O^4 \cdot 2HCl \cdot PtCl_4$ and $2(C^{30}H^{30}N^2O^4 \cdot HCl) \cdot PtCl_4$. The *acetate*, *sulphate*, *nitrate*, and *oxalate* may be prepared by treating the solution of the hydrochloride in dilute potash with the appropriate acids, and purifying the precipitates by solution in chloroform and precipitation with ether. Melting caustic potash resolves the saliceïn into salicylic acid and dimethylaniline; zinc-dust and glacial acetic acid reduce it to a colourless body. Bromine gives a colourless bromo-derivative, acetic anhydride a bright yellow acetyl-derivative, and fuming nitric acid a yellow nitro-compound. Analogous green colouring matters are formed with salicyl chloride and diethyl aniline, and methyl-diphenylamine (Fischer, *ibid.* 934).

METHYL - ANILINE - SULPHONIC ACID, $C^7H^8NSO^3 = (CH^3)HN.C^6H^4.SO^3H$. The modification of this acid obtained by the action of sulphuric acid on methylacetanilide has already been described (p. 234). Another modification is produced by heating the ethylsulphate of methylaniline to 210° , and separates on cooling from a hot aqueous solution in shining laminæ, having the composition $C^7H^8NSO^3 + H^2O$; they are very efflorescent, and insoluble in water and in alcohol. The *barium salt*, $(C^7H^8NSO^3)^2Ba + 3\frac{1}{2}H^2O$, crystallises in small shining prisms which give off their water at 110° ; the *calcium salt*, $(C^7H^8NSO^3)^2Ca + 4H^2O$, in small shining laminæ which become anhydrous at 100° ; the *lead salt*, $(C^7H^8NSO^3)^2Pb + 8H^2O$, in laminæ having a faint yellowish colour. By passing nitrous acid into the alcoholic solution of this acid, a diazo-compound is obtained, as a yellowish-white amorphous powder, which appears to have the composition $(CH^3)N-N-(SO^3)$



Dimethylaniline-sulphonic acid, $(CH^3)^2N.C^6H^4.SO^3H$. See p. 235.

METHYLANTHRACENE, $C^{15}H^{12} = C^{14}H^9(CH^3)$. This hydrocarbon is obtained: 1. By passing dimethylphenylmethane, $CH_2(C^6H^4.OH)^2$, or dimethylphenylethane, $CH_3.CH(C^6H^4.CH^3)^2$, through a red-hot tube (pp. 94, 95). 2. From the crude product of the preparation of phenanthrene. The dark-coloured masses formed in this process are freed from the greater portion of the anthracene present by fractional oxidation with potassium dichromate, then distilled in a current of steam, and recrystallised from alcohol, whereby mother-liquors are obtained, yielding, together with phenanthrene, a compound which boils above 360° , and exhibits the composition and properties of methylanthracene. It crystallises from alcohol in laminæ melting at 190° , and exhibiting a green fluorescence; is converted by heating with sodium into

a red body soluble in benzene, ether, and alcohol; and by oxidation into anthraquinone carbonic acid (p. 113) (Japp & Schultz, *Ber.* x. 1049). 3. By the action of zinc-dust at high temperatures on chrysophanic acid (p. 470); on emodin (trioxymethylantraquinone) (Liebermann, *Ber.* viii. 970); and on aloin, either from Socotrine or from Barbadoes aloes—in small quantity, however, and probably only as a secondary product (E. Schmidt, *ibid.* viii. 1275; *Arch. Pharm.* [3], viii. 496). 4. Vapour of turpentine-oil, passed through a glass tube heated to dull redness, yields a mixture of aromatic hydrocarbons, the portion of which distilling between 320° and 360° appears to contain methylantracene (G. Schultz, *Ber.* x. 84). 5. Wachendorff & Zincke (*ibid.* 1481) have obtained from aniline-residues—instead of the expected dimethylantracene—a nitrogenous body melting at 187°, and methylantracene, melting at 208°–210°, and convertible by oxidation into methylantraquinone (m. p. 160°–162°).

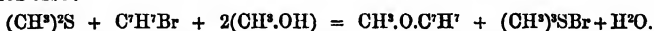
METHYL-ANTHRAQUINONE, $C^{15}H^{10}O_2$, is prepared by heating methylantracene in a water-bath with alcohol and strong nitric acid. A violent reaction then sets in, and as soon as two-thirds of the alcohol are evaporated, and a little water is added, a yellow precipitate of methylantraquinone separates out on cooling. It melts at 162°–163°, and sublimes in needles or small plates. It is moderately soluble in ether, acetone, chloroform, and boiling alcohol, sparingly in acetic acid and benzene, and crystallises from these solutions in small needles. Heated with zinc-dust and caustic soda, it gives Liebermann's anthraquinone reaction. It yields a crystallised bromo-compound, which, when heated with potash, is converted into methylalizarin, $C^{15}H^{10}O_4$, which, however, is more readily obtained by heating the quinone with fuming sulphuric acid, and fusing the resulting disulphonic acid with potash. It sublimes on heating in tufts of small needles, melting at 250°–252°, and sublimes at 200° in tufts of reddish needles. It dissolves in alkalis with a blue colour, and this solution gives blue precipitates with calcium and barium salts. It dyes mordanted cloth like alizarin, and its alkaline solution gives the same absorption-spectrum as the latter (O. Fischer, *Ber.* viii. 675).

On *Dimethylantracene* and *Dimethylantraquinone*, see vii. 84.

METHYL-BENZGLYCOCYAMINE or *Benzcreatine*, $C^9H^{11}N^2O^2$. See CREATINE (p. 579).

METHYL-BENZHYDROXAMIC ACID, $C^7H^5O.N(CH^3)OH$. See HYDROXAMIC ETHERS (p. 1080).

METHYL-BENZYL OXIDE, $CH^3.O.CH^2(C^6H^5)$, is formed by the action of benzyl chloride on potassium-methyl oxide: $C^7H^7Cl + CH^3.O.K = KCl + CH^3.O.C^6H^5$; also, together with trimethylsulphine bromide, when a mixture of 1 mol. methyl sulphide and 1 mol. benzyl bromide, diluted with methyl alcohol, is heated to 100° in a sealed tube:



It is a very mobile liquid, boiling between 168° and 170° (Cahours, *Compt. rend.* lxxx. 1317).

METHYL-BENZYL TOLYLAMINE, $N(CH^3)(CH^3.C^6H^5)(C^6H^4.CH^3)$. See TOLYLAMINES.

METHYL-BUTYL CARBINOLS, $CH^3.CHOH.C^4H^9$. See HEXYL ALCOHOLS (p. 1035).

METHYL-BUTYL KETONES. See KETONES (p. 1148).

METHYL-CARBOPIRROLIC ACID. See PYRROL-DERIVATIVES.

METHYL-CHRYsin, $C^{16}H^{12}O^4$. See CHRYsin (p. 466).

METHYL-COUMARIC ACID, $C^{10}H^{10}O^3$. Syn. with β -METHYL-ORTHOXY-PHENYLACRYLIC ACID (p. 505).

METHYL-CREOSOL, $C^8H^{12}O^2 = C^6H^2(CH^3)_2(OH)(OCH^3)$. See CREOSOL (p. 580).

METHYL-CRESOLSULPHONIC ACID, $C^8H^3(CH^3)(OCH^3)(SO^2H)$. See vii. 934.

METHYL-CRESOTIC ACID, $C^8H^3(CH^3)(OCH^3)(CO^2H)$. The potassium salt of this acid is formed by the action of potash on methylcresotate, $C^8H^3(CH^3)(OH)CO^2CH^3$ (vii. 394).

METHYL-CROTONIC ACID, $C^4H^3(CH^3)O^2$. See ANGELIC ACID (p. 86). Tiglic acid, a constituent of crotonic oil, is identical with this acid (E. Schmidt, *Ber.* x. 835).

METHYL-CYANAMIDE, $\text{CN.NH}(\text{CH}^3)$. This compound, when heated in aqueous or alcoholic solution, or exposed to the air, especially to moist air, is converted into trimethyl-melamine, $\text{C}^3\text{H}^3(\text{CH}^3)^3\text{N}^3$, identical with that which Hofmann obtained by desulphuration of methyl-thiocarbamide (p. 1271).

METHYL-DIALLYL CARBINOL, $\left. \begin{array}{c} \text{CH}^3 \\ (\text{C}^3\text{H}^3)^2 \end{array} \right\} \text{COH}$, is formed by the action of zinc on a mixture of allyl iodide and ethyl acetate. It boils at 158.4° (corr.), unites with 4 at. bromine, and forms with acetic anhydride an acetic ether boiling at 177.3° (Sorokin a. A. Saytzeff, *Deut. Chem. Ges. Ber.* ix. 34, 277).

METHYL-DICRESYLAMINE, $\text{N}(\text{CH}^3)(\text{C}^6\text{H}^4.\text{CH}^3)^2$, formed by heating dicresylamine (ditolylamine) with methyl chloride and hydrochloric acid, is an oil boiling under a pressure of 0.02 mm. at 235° – 240° (C. Girard, *Bull. Soc. Chim.* [2], xxiv. 120).

METHYL-DIETHYL-BENZENE, $\text{C}^6\text{H}^3(\text{CH}^3)(\text{C}^2\text{H}^5)^2$. See MESITYLENE, HOMOLOGUES OF (p. 1285).

METHYL-DIETHYLPHOSPHONIUM IODIDE. See PHOSPHINES.

METHYL-DIOXYAZOBENZENE, syn. with PHENYL-AZODIOXYTOLYL (*q.v.*)

METHYL-DIPHENYLAMINE, $\text{N}(\text{CH}^3)(\text{C}^6\text{H}^5)^2$. See PHENYLAMINES.

METHYL-DIPHENYLTHIOSEMICARBAZIDE, $(\text{C}^6\text{H}^5)(\text{CH}^3)\text{N.NH.NH}(\text{C}^6\text{H}^5)$. See HYDRAZINES (p. 1059).

METHYL-DIPROPYL-BENZENE, $\text{C}^{13}\text{H}^{20} = \text{C}^6\text{H}^3(\text{CH}^3)(\text{C}^3\text{H}^7)^2$. See MESITYLENE, HOMOLOGUES OF (p. 1285).

METHYLENE BROMIDE, CH_2Br_2 , heated to 140° – 150° for several hours with 15 to 20 times its bulk of water and excess of lead oxide, yields ethylene-glycol and traces of ethylene oxide, together with lead bromide (A. Jeltkow, *Ber.* vi. 558).

On the Iodide, Aceto-chloride, and Diacetate of Methylene, see vii. 807.

METHYLENE-DIBENZAMIDE, $\text{CH}_2(\text{NH.CO.C}^6\text{H}^5)^2$, is formed by treating benzonitril (2 mol.), diluted with an equal volume of chloroform, with strong sulphuric acid, and then adding 1 mol. methylal. It crystallises from alcohol in long white felted needles, and dissolves readily in carbon disulphide, ether, and chloroform; melts at 212° , and sublimes at a higher temperature almost without decomposition; burns with a smoky flame. By dilute acids it is converted into benzamide, by alcoholic potash into benzoic acid (Hepp. a. Spiess, *Ber.* ix. 1424).

METHYLENE-DISULPHONIC ACID, $\text{CH}_2(\text{SO}^3\text{H})^2$. *Disulphometholic acid. Methionic acid.*—This acid is formed by oxidising methylene thiocyanate with nitric acid. On heating the thiocyanate for a short time with a quantity of strong nitric acid just sufficient to dissolve it, immediately separating the mixture so as to expel the excess of nitric acid, then repeatedly adding water and evaporating, and finally adding barium carbonate, the barium salt, $(\text{CH}_2\text{SO}_3)^2\text{Ba}$, is obtained in crystals having a fine nacreous lustre (Julie Lermontoff, *Ber.* vii. 1282).

Methylene-disulphonic acid is also formed, together with methylamidobenzene-sulphonic acid, by heating methyl-acetanilide with sulphuric acid to 140° – 150° (at higher temperatures carbonisation takes place) as long as acetic acid is given off. On diluting the liquid with water, adding barium carbonate, and filtering the liquid while hot, the filtrate deposits the barium salt of methylene-disulphonic acid as a white crystalline powder, while the methylamidobenzenesulphonate remains in the mother-liquor. The formation of the methylene-disulphonic acid is due to the action of the sulphuric acid on the liberated acetic acid (G. A. Smyth, *ibid.* 1237).

METHYLENE-GUANAMINE. See GUANAMINES (p. 901).

METHYLENE-MERCAPTIDE or *Disulphethylmethane*, $\text{CH}_2(\text{S.C}^2\text{H}^5)^2$, formed by the action of methylene iodide on sodium mercaptide, is a colourless, fetid oil, having a density of 0.987 at 20° , and distilling without decomposition at 184° (Niederist, *Liebig's Annalen*, clxxvi. 391).

METHYL-EOSIN. See PHTHALEÏNS.

METHYL-ERYTHRIN or *Monomethyltetra-bromofluorescein*. See PHTHALEÏNS.

METHYL-ETHYL-ACETIC ACID, $\text{CH}(\text{CH}^3)(\text{C}^2\text{H}^5).\text{CO}^2\text{H}$. See PANTOIC ACIDS.

METHYL-ETHYL CARBINOL, $\text{CH}^3.\text{CHOH.C}^2\text{H}^5$. See BUTYL ALCOHOLS (p. 359).

METHYL-ETHYL KETONE, $\text{CH}_3\text{CO}\cdot\text{C}^2\text{H}_5$. See KETONES (p. 1147).

METHYL-ETHYL SULPHIDE, $\text{CH}_3\cdot\text{S}\cdot\text{C}^2\text{H}_5$. This compound, prepared by the action of ethyl iodide on sodium mercaptide, $\text{Na}\cdot\text{S}\cdot\text{C}^2\text{H}_5$, boils, according to Krüger (*J. pr. Chem.* [2], xiv. 193), at 65° – 66° (uncorr.), differing therein from the methyl-ethyl sulphide which Carius obtained by heating diethyl sulphophosphate with methyl alcohol, the corrected boiling point of which is given by Carius at $58\cdot8^\circ$ – $59\cdot5^\circ$ (vi. 598).

METHYL-ETHYL-ACETIC ACID, $\text{CH}(\text{CH}_3)(\text{C}^2\text{H}_5)\cdot\text{COOH}$. See PENTOIC ACIDS.

METHYL-ETHYL-OXAMIDE, $\text{CH}_3\cdot\text{NH}\cdot\text{CO}-\text{CO}\cdot\text{NH}\cdot\text{C}^2\text{H}_5$. See OXAMIDE.

METHYL-ETHYL-PROPYL CARBINOLS, $(\text{CH}_3)(\text{C}^2\text{H}_5)(\text{C}^3\text{H}_7)\cdot\text{COH}$. See HEPTYL ALCOHOLS (p. 1026).

METHYL-ETHYL-PROPYL-BUTYL-PHOSPHONIUM IODIDE, $(\text{CH}_3)(\text{C}^2\text{H}_5)(\text{C}^3\text{H}_7)(\text{C}^4\text{H}_9)\text{PI}$. See PHOSPHINES.

METHYL-EUGENOL, $\text{C}^{11}\text{H}^{14}\text{O}_2 = \text{C}^6\text{H}_5(\text{OCH}_3)^2(\text{C}^3\text{H}_7)$. This compound, obtained by distilling eugenol with caustic baryta, boils at 237° – 239° (Church, p. 762). The following derivatives of it have lately been obtained by Wassermann (*Compt. rend.* lxxxviii. 1206):

Bromomethyleugenol Dibromide, $\text{C}^6\text{H}_2\text{Br}(\text{OCH}_3)^2\cdot\text{C}^3\text{H}_2\text{Br}_2$, prepared by the action of bromine on a strongly cooled solution of methyl-eugenol in ether, crystallises in long, silky needles, which melt at 77° – 78° , and are soluble in alcohol and ether.

Bromomethyleugenol, $\text{C}^6\text{H}_2\text{Br}(\text{OCH}_3)^2\cdot\text{C}^3\text{H}_5$, prepared by the action of zinc-dust on a hot alcoholic solution of the preceding compound, is a colourless liquid which boils at 190° , under a pressure of 0·02 mm., and is soluble in alcohol, ether, and acetic acid.

Methyleugetic Acid, $\text{C}^6\text{H}_4(\text{OCH}_3)^2\cdot\text{C}^3\text{H}_2\text{COOH}$, obtained by the action of sodium-amalgam and chlorocarbonic ether on monobromomethyleugenol, crystallises in flat, yellowish needles, which melt at 180° , dissolve in alcohol and ether, and are slightly soluble in water.

Mercurdimethyleugenol, $(\text{C}^{11}\text{H}^{13}\text{O}_2)_2\text{Hg}$, is formed if an excess of sodium-amalgam is used in the preparation of the preceding acid. It crystallises in colourless needles, soluble in alcohol and ether, and fusing at 140° .

By heating an alkaline solution of methyleugetic acid with a solution of potassium permanganate, acidulating, and agitating the concentrated liquid with ether, a substance is obtained having the formula $\text{C}^{12}\text{H}^{12}\text{O}_3$. Its constitution is probably $\text{C}^6\text{H}_4(\text{OCH}_3)^2(\text{CH}=\text{CH}\cdot\text{CHO})\cdot\text{COOH}$. It forms colourless needles, soluble in water, and melting at 162° – 163° . In no case was any opianic acid formed.

METHYL-FERULIC ACID, $\text{C}^{11}\text{H}^{12}\text{O}_4$. See VANILLIN-DERIVATIVES.

METHYL-GLYCOLLAMIC ACIDS. Methyl-di- and methyltri-glycollamic acids are formed by heating methyl-hydantoic acid with baryta-water (p. 1045).

METHYL-GUANAMINE, $\text{C}^8\text{H}_7(\text{CH}_3)\text{N}^3$. See GUANAMINE (p. 901).

METHYL-GUANIDINE, $\text{CH}_4(\text{CH}_3)\text{N}^3$. See GUANIDINES (p. 904).

METHYL-HEXYL CARBINOL, $\text{CH}_3\cdot\text{CHOH}\cdot\text{C}^6\text{H}_{13}$. See OCTYL ALCOHOLS.

METHYL-GLYOXALINE, $\text{C}^8\text{H}_7(\text{CH}_3)\text{N}^2$. See GLYOXALINE (p. 890).

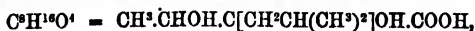
METHYL-HYDANTOÏN, $\text{C}^{11}\text{H}_9\text{N}_2\text{O}_2$. See HYDANTOÏC ACID (p. 1045).

METHYL-HYDROQUINONE. See QUINOLS.

METHYL - HYDROXYLAMINE, $\text{N}(\text{CH}_3)_2\text{H}_2\text{O}$. See HYDROXYLAMINE (p. 1081)

METHYL-ISETHIONIC ACID, syn. with OXYMETHANESULPHONIC ACID, $\text{CH}_2(\text{OH})\cdot\text{SO}^3\text{H}$ (q.v.)

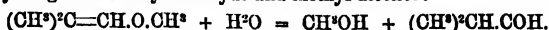
METHYL-ISOBUTYL-GLYCERIC ACID,



is formed, together with heptic acid and isobutyl acetone, by the action of alcoholic potash on ethylic bromoisobutylacetacetate (p. 1020). It is a mobile liquid which, when heated, is changed into gummy anhydrides, whilst a small portion distils over with vapour of water. Its barium salt is anhydrous, and crystallises in small needles. The calcium salt is also anhydrous, and crystallises in needles which are more soluble in hot than in cold water.

METHYL-ISOCROTYL OXIDE, $\text{C}^8\text{H}^{10}\text{O} = (\text{CH}_3)^2\text{C}=\text{CH}\cdot\text{O}\cdot\text{CH}_3$, is formed by heating isocrotyl bromide, $(\text{CH}_3)^2\text{C}=\text{CH}\cdot\text{Br}$ (vii. 401), with sodium methylate to

130°–140° for three or four hours. It is a liquid boiling at 70°–74°, and yielding, when heated to 140° for two or three hours with dilute sulphuric acid of 1 per cent., scarcely anything but isobutyl aldehyde and methyl alcohol:



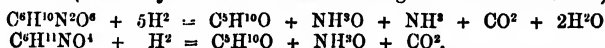
The corresponding ethyl-compound (*loc. cit.*) reacts in a similar manner (Eltetoff, *Deut. Chem. Ges. Ber.* x. 704).

METHYL-ISOPENTYL CARBINOL or **METHYL-AMYL CARBINOL**, $\text{CH}_3.\text{CHOH}.\text{CH}_2.\text{CH}_2.\text{CH}(\text{CH}_3)_2$. The preparation of this secondary alcohol from ethyl-amyl has already been noticed (p. 1025). It is also produced—together with a di-isobutylpinacene, $\text{C}_{14}\text{H}_{30}\text{O}_2$, boiling at 220°–260°—by the reducing action of water and sodium on methyl-isopentyl ketone in ethereal solution, and is obtained, after removal of the ether by distillation, as a colourless liquid of sp. gr. 0.8185 at 17.5°, boiling at 148°–150°, and not solidifying at –26°.

Methyl-is-pentylcarbinyl Acetate, $\text{CH}_3.\text{CH}(\text{OC}_2\text{H}_5\text{O}).\text{C}_5\text{H}_{11}$, obtained by heating the alcohol with acetyl chloride, is a colourless liquid boiling at 166°–168°, smelling like roses and hyacinths, having a sp. gr. of 0.8595 at 23° (water of 17.5° as unity), and boiling at 166°–168°. The *chloride*, obtained by heating the alcohol to 140° with hydrochloric acid, boils at 135°–137°. The *iodide* (which on account of its instability could not be obtained pure) heated in a reflux apparatus with dilute alcoholic potash, yields a heptylene in the form of a light very mobile oil having a pleasant odour of petroleum, and boiling at 75°–80°. This heptylene is probably a mixture of the two isomeric compounds, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2.\text{CH}=\text{CH}_2$ and $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}=\text{CH}.\text{CH}_3$ (W. Rohn, *Liebig's Annalen*, cxc. 305).

METHYL-ISOPROPYL CARBINOL, $\text{C}_5\text{H}_{12}\text{O} = \text{CH}_3.\text{CHOH}.\text{CH}(\text{CH}_3)_2$. See PENTYL ALCOHOLS.

METHYL-ISOPROPYL KETONE, $\text{C}_5\text{H}_{10}\text{O} = \text{CH}_3.\text{CO}.\text{CH}(\text{CH}_3)_2$. This ketone, first prepared by Frankland & Duppa (*Proc. Roy. Soc.* xiv. 463) by the action of baryta-water on ethylic acetodimethylacetate,—and further examined by R. Münch, who obtained it directly by the dry distillation of a mixture of calcium acetate and isobutyrate (p. 1147) is also produced: *a.* By oxidation of methyl-isopropyl carbinol (*q.v.*) *β.* Together with hydroxylamine and other products, by the reducing action of tin and hydrochloric acid on the so-called dinitroheptylic acid, $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_6$ (one of the products obtained by oxidising camphor with nitric acid), or on mononitroheptylic acid, $\text{C}_7\text{H}_{11}\text{NO}_4$ (formed by the action of sodium-amalgam on the dinitro-acid):



γ. By dehydration of isopropyl-ethyl glycol with ZnCl_2 or P_2O_5 , and of trimethyl-ethyl glycol with P_2O_5 (Flavitzky, *Ber.* x. 2240).

Methyl-isopropyl ketone boils at 94.1° (corr.), gives the iodoform reaction with iodine and potash, and forms a crystalline compound with sodium-hydrogen sulphite (Kachler, *Liebig's Annalen*, xcxi. 143).

Chlormethyl-isopropyl Ketone, $\text{CH}_2\text{Cl}.\text{CO}.\text{CH}(\text{CH}_3)_2$. See KETONES (p. 1148).

METHYL-NITROLIC ACID, $\text{CH}_2\text{NO}_2 = \text{H}.\text{CO}.\text{NH}.\text{NO}_2$. See NITROPARAFFINS, under PARAFFINS.

METHYL-NONYL KETONE, $\text{C}_{11}\text{H}_{22}\text{O} = \text{CH}_3.\text{CO}.\text{C}_9\text{H}_{19}$ (vii. 808).

METHYL-NORHEMIPINIC ACID,

METHYL-NORMECONIN,

METHYL-NOROPIANIC ACID,

} See NARCOTINE-DERIVATIVES.

METHYL-OKAMETHANE, $\text{CON}(\text{CH}_3).\text{CONH}_2$. See OXAMIC ETHERS.

METHYL-OKETHYLENE-TOLUIDINE. See TOLUIDINES.

METHYL-OXYBENZOIC ACID, $\text{C}_6\text{H}_5(\text{CH}_3)\text{OH}.\text{CO}_2\text{H}$. On the properties of the three isomeric modifications of this acid, derived from the corresponding cresols, see p. 582.

METHYL-OXYBUTYRIC ACID, $\text{C}_4\text{H}_7(\text{CH}_3)\text{O}_2$. See BUTYRIC ACIDS (OXY-) (p. 364).

METHYL-OXYPHENYL-ACRYLIC, -CROTONIC, -ANGELIC and **-PROPIONIC ACIDS**, $\text{C}_7\text{H}_7\text{O}_2$, derived from Anisic Aldehyde. See pp 504 and 505.

METHYL-OXYSULPHOBENZIDE. See OXYSULPHOBENZIDE.

METHYL-PARABANIC ACID. See PARABANIC ACID.

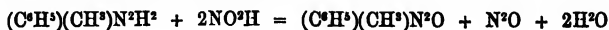
METHYL-PARAHOMOSALICYLIC ALDEHYDE. See PARAHOMOSALICYLIC ALDEHYDE.

METHYL-PENTYL CARBINOL, $\text{CH}_3\text{.CHOH.C}_5\text{H}_{11}$. See HEPTYL ALCOHOLS (p. 1024).

METHYL-PHENETHENYL KETONE, $\text{CH}_3\text{.CO.CH=CH.C}_6\text{H}_5$. See KETONES (p. 1151).

METHYL-PHENYL HYDRAZINE, $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{N.NH}_2$. See HYDRAZINES (p. 1057).

METHYL-PHENYL-NITROSAMINE, or **NITROSO-METHYL-ANILINE,** $\text{C}_6\text{H}_5\text{N}_2\text{O} = \text{C}_6\text{H}_5\text{.N(CH}_3\text{)(NO)}$, is formed, like the corresponding ethyl-compound (p. 206), by the action of nitrous acid on methylaniline dissolved in dilute hydrochloric acid, or by mixing the solutions of methylaniline hydrochloride and potassium nitrite; also, with evolution of nitrogen monoxide, by the action of nitrous acid on a salt of methylphenyl-hydrazine:



(E. Fischer, *Liebig's Annalen*, cxc. 158).

METHYL-PHENYL-SEMICARBAZIDE, $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{N.NH.CO.NH}_2$. See HYDRAZINES (p. 1058).

METHYL-PHLORETIC ACID, $\text{C}_6\text{H}_5(\text{OCH}_3)\text{.CO}_2\text{H}$. See PHLORETIC ACID.

METHYL-PHLOROL, $\text{C}_6\text{H}_5(\text{CH}_3)\text{O}$. See PHLOROL.

METHYL-PHOSPHENYL CHLORIDE, $\text{C}_6\text{H}_5\text{PClCH}_3$. See PHOSPHINES.

METHYL-PHOSPHINE, $\text{PH}_2(\text{CH}_3)$. See PHOSPHINES.

METHYL-PROPYLACETIC ACID, $\text{C}_6\text{H}_{12}\text{O}_2 = \text{CH(CH}_3\text{)(C}_6\text{H}_7\text{).COOH}$. This modification of hexoic or caproic acid, obtained from the product of the reaction of potassium cyanide on amylene hydriodide, is a liquid having a density of 0.9279 at 18° and boiling at 193°. Its silver salt separates from a hot saturated solution on cooling in needle-shaped crystals. The *barium salt* is obtained as a thick syrup, which dries up to a gummy mass. The *calcium* and *zinc salts* are less soluble in hot than in cold water; the latter is soluble in alcohol. The solution of the ammonium salt gives with *ferric chloride* a flesh-coloured precipitate soluble in excess of the iron solution. The *ethyl ether* is a liquid having a density of 0.867 at 18°, and boiling at 153° (A. Saytzeff, *Deut. Chem. Ges. Ber.* xi. 511).

METHYL-PROPYL CARBINOLS, $\text{CH}_3\text{.CHOH.C}_3\text{H}_7$. See PENTYL ALCOHOLS.

METHYL-PROPYL KETONES. See KETONES (p. 1147).

METHYL-PROPYL-CATECHUIC ACID, $(\text{C}_6\text{H}_5)(\text{OCH}_3)(\text{OC}_6\text{H}_7)(\text{COOH})$, is formed from propyl-eugenol, $\text{C}_6\text{H}_5(\text{OCH}_3)(\text{OC}_6\text{H}_7)\text{C}_3\text{H}_7$, by gradual oxidation with a hot dilute solution of potassium permanganate; and its homologues, methyl-butyl- and methyl-amyl-protocatechuic acid, are obtained in like manner from the corresponding homologues of eugenol (p. 763 of this volume).

METHYL-PYRROL, $\text{C}_4\text{H}_7\text{N(CH}_3\text{)}$. See PYRROL.

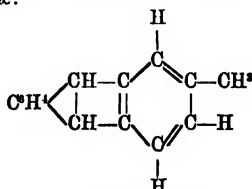
METHYL-QUININE. See QUININE. On the Sulphato-periodides of this base, see p. 491.

METHYL-QUINIZARIN, $\text{C}_{15}\text{H}_{18}\text{O}_4 = \text{C}_6\text{H}_4\text{.C}_2\text{O}_2\text{.C}_6\text{H(CH}_3\text{)(OH)}$ (Nietzki, *Deut. Chem. Ges. Ber.* vii. 2011). This homologue of Quinizarin (p. 102) is produced by heating a mixture of toluquinol (hydrotoluquinone) and phthalic anhydride in equal numbers of molecules with a quantity of sulphuric acid equal to eight or ten times the weight of the toluquinol, the heat being continued for three hours and gradually raised from 130° to 150°. The product, after boiling with water and crystallisation from benzene, is purified by boiling it with solution of sodium carbonate, and decomposing the resulting compound with an acid.

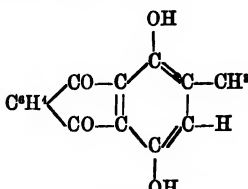
Methyl-quinizarin crystallises from alcohol or glacial acetic acid in tufts of long red needles, from dilute spirit in long capillary felted needles. It melts at 160°, and partly sublimes without decomposition. It dissolves more readily in the greater number of solvents than quinizarin, and its solutions in alkalis and in strong sulphuric acid exhibit the same absorption-bands as those of the latter. With *acetic anhydride* it forms a diacetyl-derivative, $\text{C}_{15}\text{H}_{16}(\text{C}_2\text{H}_3\text{O})_2\text{O}_4$, which crystallises in yellow needles melting at 185°.

Methyl-quinizarin distilled over heated zinc-dust yields methyl-anthracene convertible by oxidation with chromic acid into anthraquinone-carbonic acid (p. 113), together with a large quantity of anthraquinone, a circumstance in which it agrees with the only known methyl-anthracene obtained from emodin and chrysophanic acid (p. 1312).

From these results, viewed in connection with the known constitution of anthracene, and the mode of attachment of the two OH-groups and the C^2O^2 -group in quinizarin, as demonstrated by Baeyer (pp. 102, 103), it may be inferred that methyl-anthracene and methyl-quinizarin are constituted in the manner represented by the following formulæ:



Methyl-anthracene.

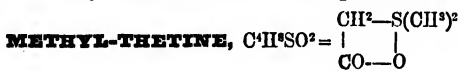


Methyl-quinizarin.

METHYL-SUCCINIC ACID, $\text{C}^2\text{H}^2(\text{CH}^3)(\text{CO}^2\text{H})^2$. See PYROTARTARIC ACID.

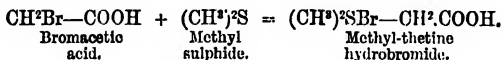
METHYLSULPHURIC CHLORIDE, $\text{CH}^3\text{O}.\text{SO}^2.\text{Cl}$. See SULPHURYL CHLORIDE.

METHYL-TETRAOXYANTHRAQUINONE, $\text{C}^{11}\text{H}^7(\text{CH}^3)\text{O}^6$. This, according to Tilden (*Chem. News*, xxxv. 273), is the constitution of an orange-yellow compound called *Aloxanthin*, which is obtained, together with a small quantity of acetic acid, by oxidising barbaloin and socaloïn with chromic acid. It melts at 260° – 265° , and may be sublimed without decomposition.



This compound, which may

be regarded as the sulphur analogue of betaine (p. 323), is obtained, in combination with hydrobromic acid, by mixing bromacetic acid and methyl sulphide in molecular proportions:



The hydrobromide is analogous in composition to betaine hydrobromide, $(\text{CH}^3)^3\text{NBr}.\text{CH}^2.\text{COOH}$. By decomposing this salt with silver oxide, or the sulphate with barium carbonate, free methyl-thetine is obtained in crystals containing 1 mol. H^2O , and exhibiting both acid and basic properties (Crum-Brown, *Deut. Chem. Ges. Ber.* vi. 1384; Crum-Brown & Letts, *ibid.* vii. 695).

Ethyl-thetine hydrobromide, prepared in like manner, is extremely deliquescent.

METHYL-THIOALDEHYDE or **THIOFORMALDEHYDE**, $\text{C}^2\text{H}^3\text{S}^2 = \text{H}^2(\text{CSH})^2$, is formed by the action of hydrogen sulphide on formaldehyde, HCOH (p. 826).

METHYL-THYMOL. See THYMOL.

METHYL-TRIBROMOGLYOKALINE. See GLYOKALINE (p. 899).

METHYL-TRIBUTYL-PHOSPHONIUM IODIDE, $(\text{CH}^3)(\text{C}^2\text{H}^5)^3\text{PI}$. See PHOSPHINES.

METHYL-TRIMERCAPTIDE, $\text{CH}(\text{S}.\text{C}^2\text{H}^5)^3$, produced by the action of chloroform on sodium-mercaptide, $\text{NaS}(\text{C}^2\text{H}^5)$, is a yellow oil which is partly decomposed by boiling, and is converted by oxidation with nitric acid into ethylenesulphonic acid (Niederist, *J. pr. Chem.* [2], xv. 174).

METHYL-VANILLIN or *Dimethyl-protocatechuic Aldehyde*, $\text{C}^8\text{H}^4(\text{OCH}^3)^2.\text{COH}$. See BENZOIC ALDEHYDE (DIOXY-), (p. 306).

METHYL-XANTHAMIDE. See XANTHAMIDE.

METHYSTICIN, syn. with KAWAIN (p. 1145).

MEYMACITE. A hydrate of tungstic acid from Moymac (Dep. Carrère), analysed by A. Carnot (*Compt. rend.* lxxix. 638). The analyses lead, after deduction of scheelite and limonite, to the formula $2\text{WO}^3.5\text{H}^2\text{O}$ or $\text{WO}^3.2\text{H}^2\text{O}$. It is evidently a decomposition-product of scheelite, probably under the influence of water containing

free acid, resulting from the decomposition of iron pyrites. The scheelite first assumes a yellow or yellowish-green colour, but retains its directions of cleavage; subsequently, however, it is converted into a soft, pure yellow, or brownish mass.

Analyses.—1 and 2. Soft, yellow to brownish, with sulphur-yellow streak. 3, Harder laminae, with yellowish streak.

WO ³	Ja ² O ³	CaO	Fe ² O ³	Mn ² O ³	H ² O	X*	Sp. gr.
71.85	1.00	2.50	6.00	0.75	12.93	4.50 = 99.53	3.80
74.25	1.05	4.65	6.10	0.65	11.75	1.85 = 100.30	
75.12	0.70	7.00	6.25	0.32	6.85	2.55 = 98.79	

* Gangue. Also traces of magnesia and sometimes of potash.

MIARGYRITE and KENNGOTTITE. *Miargyrite* is a sulphantimonite of silver, Ag²SbS₂, from Bräundorf in Saxony, containing 21.93 per cent. S, 39.14 Sb, and 36.40 Ag, together with 1.00 Cu and 0.62 Fe. Sp. gr. = 5.2 to 5.4 (m. 1010). The name *Kenngottite* was given by Haidinger to a mineral, of similar constitution but containing lead as an essential constituent. It occurs at Felsőbanya in Hungary on a quartzose rock, in monoclinic crystals, OP. + P. — P, having the angles ∞P : ∞P = 42° and 138°; has a black streak, conchoidal fracture; hardness = 2.5; sp. gr. about 6. It is somewhat brittle, melts easily before the blowpipe to a black shining globule, and, when heated for some time in the reducing flame, leaves a butter of silver amounting to 30 per cent. of the whole (Kenngott, *Annales des Mines*, 1856, [5], viii. 495).

More recently (1877) L. Sipőcz (*Liebig's Annalen*, clxxxviii. 343) has analysed *miargyrite* from Felsőbanya, where it occurs implanted on quartz-crystals, and likewise *kenngottite*, with results which show that the two minerals thus named are identical, both being sulphantimonites of silver, AgSbS₂, in which that metal is partly replaced by lead—or isomorphous mixtures of Ag²SbS₂ and PbSbS₂.

Analyses.—1 and 2, *Miargyrite*: 1. Mean of two determinations; 2. The same recalculated after deduction of copper and iron, as unessential, and replacement of the lead by its equivalent in silver (Pb = Ag²); 3 and 4, *Kenngottite*; 3. Analysis. 4. Recalculated with the same corrections as in the case of *miargyrite*. 5. Values calculated from the formula AgSbS₂.

	S	Sb	Ag	Pb	Cu	Fe	Sp. gr.
1.	21.80	40.68	32.77	4.01	0.51	0.19 = 99.96	5.273
2.	21.80	40.68	36.95	—	—	— = 99.43	to 5.322
3.	20.66	39.46	35.28	1.76	0.50	0.25 = 97.91	5.2918
4.	20.66	39.46	37.12	—	—	— = 97.24	to 5.3822
5.	21.77	41.50	36.73	—	—	— = 100	

According to A. Weisbach (*Ann. Phys. Chem.* [2], ii. 455) the crystals of *miargyrite* exhibit the axial ratio $a : b : c = 0.9865 : 2.850 : 1$. Angle $bc = 48.41'$. Weisbach also infers, from an analysis of *Kenngottite* by Richter, which gave 30.12 per cent. silver with small quantities of arsenic and lead, and a specific gravity = 5.47 at 22°, that this mineral is merely a *miargyrite* comparatively poor in silver. To the same mineral Weisbach also refers Hausmann's dull red silver ore (*fahles Rothgilligerz*) from Andreasberg, with which also Breithaupt's *Hypargyronblende* (*Hypargyrite*) is very probably identical.

MICA. The following classification of minerals belonging to the mica-group is given by Tschermak (*Jahrb. f. Min.* 1878, 71). Micæ are divided into uniaxial and diaxial, and the latter exhibit two kinds of orientation, the uniting line between the optic axes lying, in the first, in a diagonal of the hexagonal lamellæ, whilst it is perpendicular to that direction in the second. Uniaxial mica was called *biotite* by Hausmann, whilst certain micæ with small angles of the optical axes were called *phlogopite* by Dana. The diaxial micæ were all called muscovite. Non-ferruginous lithia-mica is called epidolite, and is similar to muscovite in its properties, but that containing iron (zinnwaldite) resembles phlogopite.

From the results of former investigations Tschermak arranges the micæ in the following manner:—

I.		II.	
Biotite.	Anomite.	Merxene.	Lepidomelane.
Phlogopite	—	Phlogopite.	Zinnwaldite.
Muscovite.	Lepidolite.	—	—
—	Muscovite.	—	—
—	Paragonite.	—	—
Margarite.	Margarite.	—	—

The micas in Class I. exhibit the same optical orientation, the plane of the optical axes being perpendicular to the plane of symmetry, whilst the plane of the optical axes in the micas of Class II. is parallel to the plane of symmetry. Anomite is a rare mica with peculiar chemical composition. Meroxene is the name given to all Vesuvian micas. Tschermak concludes that *all micas belong to the monosymmetrical* (monoclinic) system, and that their twin-formation leads to the assumption of a system of axes which is characterised by the two axes in the plane of symmetry intersecting each other almost at an angle of 90° . This last peculiarity accounts for the rhombic types at one time and rhombohedral types at another time observed to occur in these micas (iii. 1010). The optical relationships of the micas is given in the following table, the dispersion being stated in the usual manner (ρ denoting red and ν violet light), and in addition $+f$ signifies that the positive optical axis angle is rendered greater by an increased amount of iron in the mineral, and $-f$ that the same angle is diminished by an increase of iron:—

I.			II.		
Anomite	.	$\rho > \nu + f$.	Meroxene	.	$\rho < \nu - f$.
Lepidolite	.	$\rho > \nu$	Phlogopite	.	$\rho < \nu - f$.
Muscovite	.	$\rho > \nu + f$.	Zinnwaldite	.	$\rho < \nu - f$.
Paragonite	.	$\rho > \nu$			
Margarite	.	$\rho > \nu$			

From this table it appears that with micas of Class I. the dispersion is generally $\rho > \nu$ up to margarite, and with the micas of Class II. $\rho < \nu$ up to zinnwaldite. In all these cases no relationship can be traced between the chemical and optical properties, a fact which agrees with Tschermak's observations in respect to augite and bronzite.

N. v. Kokscharow, on the other hand (*Jahrb. f. Min.* 1877, 798), regards all micas without exception as belonging to the orthorhombic system, with the angle $\infty P : \infty P \infty$ exactly equal to 120° , their monoclinic character of symmetry being only apparent. The axial ratio $a : b : c$ is $1 : 1.73205 : 2.84953$, or $0.57735 : 1 : 1.64618$. Twins are formed according to the two laws: Twin-plane ∞P or $c \perp P$.

H. Baumhauer (*Münch. Akad. Ber.* 1874, 245; *Ja'resb. f. Chem.* 1875, 2) infers from an examination of the corrosion-figures produced on potash-mica and magnesia-mica by the action of a hot mixture of fluorspar and sulphuric acid, that the former belongs to the monoclinic, the latter to the rhombohedral system.

G. vom Rath (*Pogg. Ann.* clviii. 420) describes a six-sided plate of mica with re-entering edges (from Vesuvius) as a twin of the combination $\frac{1}{2}P2 . \infty P2 . 0P$, according to the law: Twin-axis normal to $0P$; angle of rotation 120° . Tschermak (*Min. Mitt.* 1876, 87) describes twins of biotite from Vesuvius as belonging to the monoclinic system.

Potash-mica. Muscovite.—According to M. Bauer (*Berl. Akad. Ber.* 187 684; *Jahrb. f. Min.* 1878, 310), the micas of this variety are monoclinic, the plane of the optic axes being perpendicular to the plane of symmetry, the optic median line forming with the cleavage-face an angle of $88^\circ 18'$ and the angle of the optic axes being equal to $40^\circ 21'$.

	1	2	3	4	5	6	7	8
Fluorine	0.12	not det.	0.15	2.06	2.16	—	—	—
Silica	45.61	45.81	45.57	47.01	46.46	48.76	58.64	40.77
Alumina	36.36	36.78	36.72	32.46	32.76	29.91	25.00	15.69
Ferric Oxide	1.33	1.05	0.95	—	—	4.24	5.11	26.55
Ferrous Oxide	1.07	not det.	1.28	4.42	4.01	0.41	—	0.78
Magnesia	0.66	0.77	0.38	1.05	1.03	2.63	2.11	5.89
Lime	0.46	not det.	0.21	—	—	0.33	0.61	0.86
Lithia	—	—	0.19	—	trace	—	—	—
Potash	not	9.22	8.81	8.86	8.86	6.83	5.14	5.07
Soda	det.	0.79	0.62	1.56	1.56	2.31	1.31	1.40
Water	4.93	4.72	5.02	3.44	3.44	4.60	2.08	2.32
	—	—	99.93	100.86	100.28	100.02	100.00	99.23
Specific Gravity	2.830	—	2.846	—	—	2.7745	—	2.967

No. 4 contains traces of lithia; No. 5 traces of titanio oxide.

Analyses.—1 and 2, from India, analysed by L. Sipöcz. 3. From Bengal, by S. Blau (Ludwig, *Jahrb. f. Min.* 1874, 84). 4 and 5. White, from the granitic gneiss of New York (P. Schweizer, *Amer. Chemist*, iv. 445). 6. Light-brown transparent plates mixed with oligoclase and orthoclase, distinguished by its large amount of sodium and silicon; locality not stated (Löbisch, *Min. Mitt.* 1877, 271). 7. Mica from the eclogite of Saxony (E. v. Gerichten, viii. 703). 8. Mica from the hornblende andesite of Transylvania, analysed by K. John (viii. 1043).

Lithia-mica. 1. *Lepidolite* from Paris, Maine, having a larger grain, and finer lilac colour than the following. 2. *Lepidolite* from Rozena, in Moravia. Bunsen a. Kirchoff found in this mineral 0.24 per cent. rubidium, which must be deducted from the amount of potash in the analysis given below: the spectroscope showed also a trace of cesium. 3. *Zinnwaldite*, from Zinnwald, in Bohemia; rubidium and cesium were detected in it spectroscopically; thallium has not been found either in this or in any other lithia-mica (Berwerth, *Jahrb. f. Min.* 1877, 830; 1878, 316). 4. Mica from the neighbourhood of Portland and Middletown, Connecticut, distinguished by its large amount of ferrous oxide and by the presence of lithium, the latter being recognisable by the colour which it gives to the blowpipe flame. This mineral is found in granitic veins in gneiss and mica-slate; it is optically uniaxial (?), and intimately intergrown with muscovite. The numbers under (4) are the mean of two analyses:

	1	2	3	4
Fluorine	5.15	7.88	7.94	0.76*
Silica	50.39	50.98	45.87	35.61
Titanic Oxide	—	—	—	1.46
Alumina	28.19	27.80	22.50	20.03
Ferric Oxide	—	—	0.66	0.13
Ferrous Oxide	—	0.05	11.61	21.85
Manganous Oxide	trace	trace	1.75	1.19
Magnesian	—	—	—	5.23
Lithia	5.08	5.88	3.28	0.95
Potash	12.34	10.78	10.46	9.69
Soda	—	—	0.42	0.52
Water	2.36	0.96	0.91	1.87
Phosphoric Anhydride	—	0.05	0.08	—
	103.51	104.38	105.48	99.29
Deducting O equiv. to F	2.17	3.32	3.34	0.32
there remains	101.34	101.06	102.14	98.97
Specific gravity	2.8546	2.834	2.9715	2.96

* Loss by ignition.

Magnesia-micas (see next page).

	1	2	3	4	5	6	7
Silica	40.81	38.49	40.24	39.30	40.34	49.44	39.55
Titanic Oxide	—	—	0.56	—	—	—	—
Alumina	16.47	14.43	12.92	16.95	15.14	26.05	15.95
Ferric Oxide	2.16	5.44	7.67	0.48	2.20	—	7.80
Ferrous Oxide	5.92	14.75	2.15	7.86	0.77	2.62	—
Manganous Oxide	—	—	—	0.69	—	0.29	—
Magnesian	21.08	16.35	23.29	21.89	27.97	3.03	22.25
Baryta	—	—	—	—	2.46	5.76	—
Lime	—	—	0.35	0.82	—	1.81	—
Potash	9.01	8.12	} not det. {	7.79	7.07	7.54	} 10.35
Soda	1.55	0.33		0.49	2.58	—	
Water	2.19	0.89	0.68	4.02	3.21	4.24	4.10
Fluorine	trace	trace	—	0.89	0.82	—	—
	99.19	99.00	—	101.08	102.56	100.18	100
Specific gravity	—	3.004	—	2.864 at 16°	2.959 at 16°	2.83 at 10°	2.84

Magnesia-micas. 1. *Phlogopite*, occurring, together with apatite, at Oedegarden, in Norway. Colour by reflected light, dark-reddish brown; by transmitted light, rose-red in thick, yellow in thinner laminae. Optically biaxial (Bröggen a. Reusch, *Jahrb. f. Min.* 1876, 196). 2. Mica from Vesuvius; blackish plates, implanted together with vesuvian or limestone (Berwerth, *ibid.* 1877, 830; 1878, 316). 3. *Barytic Phlogopite*, from Edwards, St. Lawrence County, New York; brown translucent plates. 4. *Barytic Mica*, occurring imbedded in thin white layers in the emerald-bearing mica-slate of the Habach-thal, Salzburg; rhombic, with the faces ∞P and OP ; cleaving very easily in the direction of the latter (Sandborger, *ibid.* 1875, 624). 5. *Euchlorite* from Chester, Massachusetts (Pisani, *Compt. rend.* lxxxiii. 166).

MICA-PORPHYRY. See PORPHYRY.

MICA-SLATE. On the mica-slate region of the Saxon Erzgebirge, see Kalkowsky (*Zeitschr. geol. Ges.* xxviii. 682; *Jahresh. f. Chem.* xxviii. 682).

MICA-TRAPP. On the mica-trapp of Metzdorf, near Oederan in Saxony, see Kalkowsky (*Jahrb. f. Min.* 1875, 488).

MICROLINE. Triclinic felspar containing from 11 to 16 per cent. potassium and only a small proportion of sodium (see FELSPAR, p. 775).

MICROLITE. See TANTALATES.

MICROSOMMITE. A mineral discovered by Scacchi (*Jahresh. f. Chem.* 1873, 1147) in the pores of blocks ejected from Vesuvius in the eruption of April 1872, and further examined by G. vom Rath (*Jahrb. f. Min.* 1873, 544) and by Rammelsberg (*Berl. Acad. Ber.* 1876, 699). It has probably been formed by the action of volcanic vapours charged with sodium chloride on the leucites and augites of the lavas. It is accompanied by iron-glance. The crystals, which are extremely small (1500 weighing only about 0.1 grm.), belong to the hexagonal system, and exhibit the combination $\infty P.OP$, sometimes with P ; angle of the middle edge = 43.40° , whence the ratio of principal axis to the secondary axes is 1 : 2.88. Hardness = 6. Sp. gr. = 2.6 at 15° . From the results of an analysis (A) made with a very small quantity of substance, vom Rath deduces the formula $(\frac{2}{3}K^2O.\frac{2}{3}CaO).Al^2O^3.2SiO^2 + NaCl + \frac{1}{15}(CaO.SO^3)$, which gives the values B, agreeing nearly with the analytical numbers, excepting that the percentage of sodium found is somewhat greater than the calculated value, indicating that the sodium is present only as NaCl.

SiO ²	Al ² O ³	CaO	K ² O	Na	Cl	SO ³
33.0	29.0	11.2	11.5	6.5	9.1	1.7 = 102
33.0	28.3	10.5	10.4	6.3	9.8	1.7 = 100

Microsommitte is therefore a member of the sodalite group, nearly related crystallographically to nephelin (vom Rath).

According to Rammelsberg, the crystals of microsommitte are identical in form with nephelin, and consist of a mixture of two substances, one of which contains sulphuric acid, while the other is free from it. The remaining constituents, SiO², Al²O³, CaO, Na²O, K²O, Cl, are the same for both. The silicate of the former is $R^2Al^2Si^2O^{10}.2CaAl^2Si^2O^8$, while that of the latter, which contains chlorine without sulphuric acid, is $R^2Al^2Si^2O^{10}.2CaAl^2Si^2O^8$.

MILARITE. This mineral, from Graubünden, Switzerland, first analysed by Kenngott, who regarded it as a zeolite, and afterwards by Frenzel, who assigned to it the formula $3R^2O.CaO.Al^2O^3.18SiO^2$, regarding the water as basic (vii. 809), has been further analysed by Finkener (*Jahrb. f. Min.* 1874, 61), who finds it to contain :

SiO ²	Al ² O ³	CaO	MgO	K ² O	Na ² O	H ² O	Sp. gr.
70.04	11.62	10.05	0.20	2.74	0.65	1.69 = 99.99	2.5

and by E. Ludwig (*ibid.* 1878, 411), who obtains the numbers given under A, which agree nearly with those found by Finkener, and may be represented by the formula $HKCaAl^2Si^2O^{10}$ or $H^2O.K^2O.2CaO.2Al^2O^3.24SiO^2$, which gives the values B :

	SiO ²	Al ² O ³	CaO	MgO	K ² O	Na ² O	H ² O
(A.)	71.81	10.67	11.65	trace	4.86	trace	1.36 = 100.35
(B.)	72.66	10.39	11.30	—	4.74	—	0.91 = 100

Sp. gr. = 2.5529.

According to Tschermak, the crystals, apparently hexagonal, are really rhombic intersection-twins according to ∞P , and exhibit the faces ∞P , ∞P_3 , $3P_3$, OP .

MILK. Composition. 1. Of Human Milk. The following results have been obtained by Brunner (*Pflüger's Archiv. f. Physiologie*, vii. 445), and Christenn (*Landw. Vers. St.* xx. 439):

	Brunner	Christenn
Total Solids	—	12·75
Water	90·00	87·24
Fat	1·73	4·23
Sugar	6·23	5·96
Proteids	0·63	1·90
Soluble salts	1·41 salts	0·28

For the methods of analysis, see p. 1326.

Analyses of the Milk of women of different ages have been published by H. Gerber (*Bull. Soc. Chim.* [2], xxiii. 342):

Age	33 years	32 years	23 years	27 years	25 years	23 years
Water	88·02	86·22	84·86	86·62	87·57	93·17
Butter	2·90	4·54	5·23	4·64	3·44	2·15
Casein and Albumin	1·60	2·81	2·74	2·03	2·03	1·06
Sugar	7·03	5·96	6·40	6·46	6·27	3·46
Salts	0·31	0·41	0·75	0·22	0·67	0·14
Reaction	slightly acid	neutral	neutral	alkaline	poutral	neutral
Sp gr.	1·0272	1·031	1·029	1·028	1·031	1·0215

H. A. Mott (*Amer. Chemist*, vi. 364) finds that the milk of women of African race is richer in solid constituents than that of women of the Caucasian race.

2. Cows' Milk. The following results have been obtained by Gerber (*loc. cit.*) as the mean of four analyses, and by C. A. Cameron (*Chem. News*, xxxi. 54) as the result of forty analyses, of the milk of cows from Dublin dairies:

	Water	Fat	Proteids	Sugar	Salts	Sp. gr.
Gerber	86·21	4·18	4·43	4·28	0·86 =	99·96
Cameron	87·00	4·00	4·10	4·28	0·62 =	100

Stevenson Macadam (*American Chemist*, v. 419; vi. 30) has analysed 66 samples of the milk of 46 cows from dairies in Edinburgh, and 7 samples from a farm where the cows were fed on good pasturage, with the following mean results:

	Edinburgh milk	Milk from the farm
Total of Solid Constituents	12·27	12·77 p. c.
Fat	2·58	2·88
Ash	0·71	0·71

From the individual analyses, Macadam concludes that the quality of the milk is affected by that of the fodder and the amount of water contained therein, by the season, the temperature of the cow-house, the race, age, and health of the cow, and the time of calving. Unadulterated milk from town dairies should have a density not less than 1·03, and should contain:

Cream not less than	6	vol. per cent.
Solids	11	"
Fat	2	"
Salts	0·65	"

F. N. Macnamara (*Chem. News*, xxvii. 273) has analysed the milk of small Bengal cows, whose daily food usually consists of about 12 lbs. of rice-straw, 2½ oil-cake, 1 lb. rice-husks, the water in which the rice for the family has been boiled, and 35 lbs. of water. The following are the results:

Milk of Bengal Cows.

	Age of calf	Daily yield of milk	Evaporation-residue of the milk	Casein	Sugar	Fat	Salts
1.	1 month	6½ lb.	15.12	5.50	3.98	4.98	0.76 p. c.
2.	2 "	5 "	12.82	4.30	4.40	3.60	0.70 "
3.	2½ "	5 "	15.28	5.76	4.10	4.10	0.84 "
4.	5 "	4 "	11.90	4.30	4.37	2.52	0.78 "
5.	6 "	10 "	12.04	4.30	4.10	3.20	0.70 "
6.	7 "	5 "	11.65	5.40	3.86	1.90	0.82 "
7.	10 "	4 "	11.92	4.20	4.37	3.00	0.68 "
8.*	2 "	—	15.90	7.76	3.40	4.10	0.90 "

* This cow was milked only every second or third day.

Voelcker (*Chem. News*, xxxii. 26) has analysed the morning and evening milk from the farm of the Royal Agricultural College at Cirencester, for the several months of the year 1863, with the following results:

		Jan.	Feb.	March	April	May	June	July	Sept.	Oct.	Nov.	Dec.
Water	Morning	87.70	87.50	88.60	87.50	88.20	87.30	88.70	89.01	87.60	87.10	86.70
"	Evening	87.40	86.40	88.16	89.00	87.80	87.30	87.80	90.70	90.30	86.20	86.00
Butter	Morning	2.60	2.58	2.71	3.15	2.42	3.05	2.22	1.99	3.90	3.41	3.74
"	Evening	2.28	2.53	2.96	3.47	2.71	2.94	3.61	1.70	2.99	3.78	4.12
Casein and Albumin	Morning	2.94	3.44	2.43	2.94	3.12	3.00	2.94	2.94	2.87	2.94	2.87
"	Evening	2.87	3.37	2.62	2.69	2.87	2.87	2.81	2.81	2.37	3.19	3.62
Milk-sugar	Morning	5.82	5.44	5.35	5.60	5.49	5.89	5.38	4.58	4.84	5.41	5.92
"	Evening	6.56	5.66	5.55	5.08	6.85	6.05	6.10	4.04	3.76	5.68	5.46
Ash	Morning	0.94	1.04	0.91	0.81	0.77	0.76	0.76	0.64	0.79	1.14	0.77
"	Evening	0.89	1.14	0.77	0.78	0.77	0.84	0.68	0.66	0.58	1.15	0.80

E. L. Cleaver (*Pharm. J. Trans.* [3], iv. 973) has examined the changes produced in the amount of the solid constituents of milk by keeping. For this purpose, a quantity of milk drawn from the cow on April 30 was divided into several portions, one of which was analysed immediately, the others at the dates mentioned below:

	Total solids	Fat	Ash
April 30	12.48	3.6	0.7
May 1	12.37	3.6	0.7
" 2	12.18	3.6	0.7
" 4	12.12	3.6	0.7
" 6	12.09	3.6	0.7
" 8	12.07	3.6	0.7
" 12	11.97	3.52	0.7
" 18	11.97	3.4	0.7

A careful examination of the milk of cows both in health and in disease has lately been made by A. Wynter Blyth (*Chem. Soc. J.* 1879, xxxv. 530), whose analyses give for the average composition of healthy cows' milk:

Water	Fat	Sugar	Casein	Albumin	Galactin	Bitter principle	Ash
86.87	3.50	4.00	3.98	0.77	0.17	0.01	0.70

besides a nitrogenous colouring matter called *lactochrome*, the quantity of which was not determined, and traces of creatine and urea.

Galactin is described as a nitrogenous substance (regarded by Blyth as an alkaloid) which is precipitated, together with *lactochrome*, from the whey by mercury nitrate, after the casein and albumin have been completely removed. On decomposing the mercury precipitate with hydrogen sulphide, and treating the filtrate (freed from excess of H₂S) with lead acetate, a lead-compound of galactin is thrown down; and this, when decomposed by hydrogen sulphide, yields a solution from which, by evaporation, the galactin is obtained in the form of a white, brittle, neutral, tasteless, non-crystalline

mass, soluble in water, insoluble in alcohol, and giving precipitates with sodium phosphomolybdate and metatungstic acid. The composition of galactin appears, from the analysis of its lead compound, to be $C^{14}H^{12}N^4O^{14}$.

The filtrate from the galactin precipitate, freed from excess of lead by hydrogen sulphide and treated with mercury nitrate, yields a precipitate of the mercury-compound of lactochrome, the composition of which is stated to be $HgO.C^9H^{10}NO^8$ (?), and from this precipitate the lactochrome may be separated in the form of bright orange-red, resin-like masses, softening at 100° , very soluble in water and in hot alcohol, but separating partially as the liquid cools. Strong solutions give a simple spectrum, allowing most of the red and yellow rays to pass through.

From analyses of the milk of diseased cows, Blyth infers that a cow suffering even from very acute disease (phthisis, pneumonia, congested liver, &c.) may give milk differing in no essential particular from normal milk, whereas local affections of the udder, characterised by bloody or purulent deposits, may easily be recognised by the presence of such products in the milk. The milk of a cow attacked by cattle-plague was, however, found by Blyth (*Chem. News*, 1875, xxxii. 244) to differ considerably in composition from normal milk, as the following numbers will show :

	Water	Fat	Casein	Sugar	Ash
Average normal milk . . .	87.550	3.070	4.160	4.760	0.730 p. c.
Milk 1st day of sickness . . .	91.239	0.390	2.899	4.809	0.663 "
" 2nd " " . . .	79.903	5.010	14.380		0.707 "
" " " " . . .	86.320	3.838	9.135		0.707 "
" 3rd " " . . .	87.676	0.891	3.948	7.152	0.333 "
" 4th " " . . .	83.852	7.798	3.469	4.669	0.212 "
" 5 " " " . . .	87.900	1.062	10.376		0.662 "
" 7 " " " . . .	86.067	1.587	10.849		0.507 "
" 14 " " " . . .	83.882	3.961	11.478		0.679 "

The milk of the diseased cow contained organised structures which were not present in normal milk, and the globules of the butter-fat had a strong tendency to agglutinate.

According to W. Fleischmann (*Dingl. pol. J.* cxxiv. 461), 100 kg. of milk, after being left at rest for twenty-four hours for the cream to separate, and then treated by the ice process, yield the following quantities of the several constituents :

Kilograms		
20.00 Cream		<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 2em; vertical-align: middle; margin-right: 5px;">{</div> <div> 3.56 Butter 16.30 Butter-milk 0.14 Loss 7.93 Curd </div> </div>
79.70 Skimmed milk		<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 2em; vertical-align: middle; margin-right: 5px;">{</div> <div> 71.45 Whey 0.32 Loss 0.30 Loss </div> </div>
0.30 Loss		
100		100

The percentage composition of fresh cows' milk, and of its products, primary and secondary, was found by Fleischmann to be as follows :

	Water	Fat	Casein	Albumin	Milk-sugar	Ash
Whole Milk	87.60	3.98	3.02	0.40	4.30	0.70
Cream	77.30	15.45	3.20	0.20	3.15	0.70
Skim-milk	90.34	1.00	2.87	0.45	4.63	0.71
Butter	14.89	82.02	1.97	0.28	0.28	0.56
Butter-milk	91.00	0.80	3.50	0.20	3.80	0.70
Curd	59.30	6.43	24.22	3.53	5.01	1.51
Whey.	94.00	0.35	0.40	0.40	4.55	0.60

The division of the individual constituents of the milk between the several products is represented by the following numbers :

Composition of Cows' Milk.

	Water	Fat	Casein	Albumin	Milk-sugar	Ash
Butter . . .	2	73	6	4	1	5
Butter-milk . .	17	7	20	8	14	17
Curd . . .	5	14	64	70	10	17
Whey . . .	76	6	10	18	75	61

3. *Milk of other Animals.*—The milk of sheep and goats has been analysed by Macadam (*Pharm. J. Trans.* [3], iv. 959); that of mares and sows by Cameron (*Chem. News*, xxxi. 54):

	Water	Fat	Proteids	Sugar	Ash
Mare . . .	90.310	1.055	1.953	6.285	0.397
Sow . . .	81.760	5.830	6.180	5.335	0.895
	Total Solids		Fat	Ash	
Sheep . . .	17.78		5.72	0.94	
Goat . . .	13.43		4.31	0.73	

M. Schrodtt (*Landw. Versuchs.-St.* xxiii. 311) found in the milk of a five-years' old mare, ten weeks after foaling, 8.85 per cent. of dry substance, consisting of 1.27 fat, 1.50 proteids, 5.75 milk-sugar, and 0.37 ash. The fresh milk was perfectly neutral.

J. Duval found in fresh mares' milk an acid different from hippuric acid, which he designates as equinic acid (p. 736).

Reaction of Milk with Litmus, &c.—The most contradictory statements have been made as to the reaction of normal fresh cows' milk with litmus, some observers having found the reaction of milk to be acid, while others describe it as alkaline. Soxhlet considers that milk possesses what he calls an *amphoteric* or *amphigenic* reaction, i.e. that it has the remarkable property of turning simultaneously red litmus blue and blue litmus red; and this arises from the fact that milk contains both acid and neutral phosphates of the alkali-metals. Heintz maintains that a fluid containing both acid and ordinary alkaline phosphates simply imparts a violet colour to red and blue litmus paper.

A. Vogel (*J. pr. Chem.* [2], viii. 137) uses, instead of litmus-paper, a carefully prepared neutral tincture of litmus, and, as the results of his experiments, states that he has never yet found freshly drawn cows' milk with a decided alkaline reaction. When litmus-tincture which has been reddened by milk is left exposed to the air in a watch-glass, it gradually loses the red colour and passes into blue, whereas if it be closely corked up, it retains the red colour, though in some cases it seemed to become slightly blue in the course of an hour or two. In either case it acquires after three or four days a deep red, owing to the formation of lactic acid. Hence it follows that normal fresh cows' milk contains no free lactic acid. Litmus-tincture reddened by milk also becomes blue if shaken up and poured backwards and forwards from one vessel to another, and more especially on heating. Vogel thinks that the restoration of the blue colour in these cases is due to the escape of carbonic acid which fresh milk contains. Soxhlet also found that milk, when subjected to the action of the air-pump, gave up carbonic acid, and became decidedly alkaline. Other tests for alkalinity in liquids were also applied by Vogel to milk, with negative results.

Out of the milk of 30 cows which was examined by Bischoff at Schleisheim, only two specimens showed the double reaction with certainty. In the greater number of cases the reaction was either neutral or transiently acid. Some specimens, however, gave at first a weak alkaline reaction, quickly passing into acid. This effect may have been due to the absorption of ammonia by the milk, as the experiments were made in the stalls.

Fermentation of Milk.—E. Reichardt (*Arch. Pharm.* [3], v. 210) observes that milk-sugar in contact with yeast at 30° passes into alcoholic fermentation. This observation explains the fermentation of mares' milk, which is utilised in the warm climate of Asia for the preparation of alcoholic drinks, such as Koumiss, and likewise points out the means of preventing the spontaneous fermentation of milk, by cooling it rapidly, keeping it in cool places, and protecting it from contact with dough or fermenting liquids, by which yeast-germs might be introduced into it.

E. Tisserand (*Compt. rend.* lxxxii. 266) observes that the nearer milk is brought to the temperature of 0° C., the more quickly does the cream rise to the surface, and the more complete is the separation, so that the yield of butter is thereby increased;

moreover, both the butter and the cheese are improved in quality by exposure to low temperatures during their preparation, probably in consequence of the effect of the cold in arresting the development of organisms which excite fermentation.

According to Soxhlet (*Dingl. pol. J.* cccxiii. 329), milk cooled by ice-water remains sweet and unaltered for fourteen days, but afterwards gradually acquires a rancid taste, and after twenty-eight days becomes coagulable by boiling, in consequence of the presence of acids formed by oxidation of the milk-fat; after thirty-four days it was found to coagulate even in the ice-water.

Observations on the use of *Salicylic acid* as an antiseptic in dairy operations have been published by Manetti a. Musso (*Ber.* ix. 1438; *Pharm. J. Trans.* [3], vii. 175).

On the use of Boric acid for preserving milk, see Hirschberg (*Arch. Pharm.* [5], 520).

Coagulation of Milk.—According to Béchamp (*Compt. rend.* lxxvi. 654, 836), the coagulation of milk is due to the peculiar physiological activity of *microzymes*, which are present in normal milk, and simultaneously excite alcoholic, acetic, and lactic fermentation, whether they have been previously developed into bacteria or not. Recently drawn cows' milk contains alcohol and acetic acid, the quantities of which increase in the curdled milk. Matthieu a. Urbain, on the other hand, attribute the coagulation of milk to a process of oxidation, and the consequent formation of acids.

The observation of Schwalbe (vii. 811), that the curdling of milk is prevented by *oil of mustard*, has been confirmed by A. Vogel (*N. Rep. Pharm.* xxiii. 505), who finds that this compound greatly retards the formation of lactic acid. *Bitter almond oil* and *cinnamon oil* likewise retard the formation of acids, but in a much lower degree than mustard-oil. Turpentine-oil, clove-oil, benzin (light petroleum), phenol, carbon disulphide, and hydrogen sulphide, added in the proportion of 1 drop to 20 grams of milk, produce scarcely any retarding action. Schwalbe's observation that casein is converted by mustard-oil into albumin has not been confirmed by Vogel.

According to Schreiner (*Landw. Versuchs.-St.* xxii. 60), boiled milk does not coagulate spontaneously so soon as unboiled milk; whilst, on the contrary, boiled milk requires 10 to 12 per cent. more acid to coagulate it than unboiled milk does. The amount of rennet which serves to curdle fresh milk is insufficient to curdle one-tenth the amount of boiled milk, even when applied ten times as long, and at the same temperature (35° C.) The time required for spontaneous coagulation of fresh milk, and the amount of acid required to produce the same effect, depend on the amount of solids in the milk. Unboiled milk treated with rennet curdles the sooner, the less the amount of total solids. The amount of acid required to coagulate milk from the same animal increases in the time from the last calving up to the subsequent dry period, with the increase of the total solids during the lactation period. Milk from Friesland cows gave during this time an increase of solids of from 11 to 13 per cent., whilst that from Simmenthal cows gave an increase from 12 to 16 per cent. Crosses between the two breeds gave milk which sometimes approached the one, and sometimes the other in the amount of increase. Milk, when boiled, evolves hydrogen sulphide which may be easily detected in the usual way.

Dialysis of Milk.—When milk is subjected to dialysis through sized paper, the casein remains on the dialyser in the form of a finely divided precipitate insoluble in soda-ley, acetic acid, and in the concentrated diffusate of the milk, whence it appears to have undergone alteration. If the dialysis be allowed to go on for about thirty hours, and the inner liquid be then filtered, a neutral solution of casein is obtained nearly free from fat, containing only small quantities of the phosphates of magnesium and calcium, and yielding on acidulation a precipitate of casein: the soluble salts, therefore, contribute nothing to the retention of the casein in solution in the milk. If the dialysis be continued for a longer time, the casein becomes insoluble, and the diffusate contains a little albumin, together with a nitrogenous crystalloid substance which Schmidt regards as the solvent of the casein and of the calcium phosphate. Casein, precipitated by acetic acid from diluted milk, washed with water, dissolved in soda-ley, and freed from fat by ether, gave by dialysis a neutral liquid, yielding on acidulation a precipitate of casein which dissolved in the concentrated milk diffusate. Casein is therefore insoluble in water, but is retained in solution in milk through the agency of certain nitrogenous bodies. Casein, precipitated in consequence of spontaneous acidulation, dissolves in the diffusate of milk; casein precipitated by rennet does not.

Milk contains a ferment which converts milk-sugar into lactic acid, and therefore plays an important part in the spontaneous coagulation of milk. The coagulation produced by rennet takes place even in the alkaline liquid, so that the acid plays merely an auxiliary part in the coagulation (*Al. Schmidt, N. Rep. Pharm.* xxiv. 315).

Milk Analysis. The following method is given by Ritthausen (*J. pr. Chem.* [2], xv. 329; xvi. 314). The milk, diluted with 20 pts. of water, is precipitated by a solution of cupric sulphate, and the corresponding quantity of caustic potash or soda-ley; the precipitate, which contains all the proteïds and all the fat, is collected on a weighed filter, and the filtrate is used for estimating the milk-sugar by Fehling's process. The fat is extracted from the copper precipitate by ether and estimated, and the copper precipitate, after final washing with alcohol, is dried, weighed, and ignited, the loss of weight on ignition being reckoned as protein-substance. Ritthausen finds in milk a very small quantity of a carbohydrate different from milk-sugar, and exhibiting some resemblance to dextrin.

G. Christenn (*Landw. Versuchs.-St.* xx. 439) has discussed the several methods which have been proposed for the analysis of milk, and gives the preference to that of Haidlen (iii. 1015), which may be applied to the analysis of the milk of any animal. It consists in mixing the milk with one-fifth of its weight of finely powdered gypsum, evaporating to dryness at 110°, and weighing the residue, the loss giving the amount of water, and the weight of the residue, *minus* the gypsum, giving the weight of solid constituents. The fat is then extracted from this residue by ether, then the milk-sugar and soluble salts by alcohol of 85 per cent. The last residue contains the albuminoids and insoluble salts, the weight of which is equal to that of this residue after deduction of the gypsum. The quantities of the soluble and insoluble salts are determined in the usual manner, and the weight of the latter deducted from that of the last residue gives the amount of the albuminoids.

The alterations in this method, proposed by Christenn, are: 1st, to add powdered glass instead of plaster of Paris* to the milk before evaporating to dryness, in order to avoid errors arising from the hygroscopic nature of the plaster of Paris, and from the solubility of this substance in dilute alcohol. This latter source of error gives too high results for the sugar, at the expense of the albuminoids. 2nd, to dry the residue at 95°–100° instead of 110°.

The following process, devised by Christenn, also gives satisfactory results, closely agreeing with those obtained by Haidlen's method. 10 grams of milk are mixed with 10 c.c. of ether and 20 c.c. of alcohol; the mixture is well stirred; and the precipitated albuminoids are collected on a weighed filter, and washed with a mixture of 1 part of ether and 2 of alcohol, until the filtrate, which is at first turbid, begins to run through clear. The precipitate, dried at 95°–100°, gives the weight of albuminoids and insoluble salts; and the weight of the latter is obtained by ignition. The filtrate evaporated to dryness gives the amount of fat, soluble salts, and milk-sugar; the fat is extracted with ether, the residue weighed, and the fat determined by difference. The mixture of soluble salts and sugar is ignited, and the residue treated with hot water. The weight of soluble salts is obtained by evaporating the aqueous solution to dryness and igniting.

Estimation of Fat.—Macnamara (*Chem. News*, xxvii. 242) encloses 10 c.c. milk and an equal volume of ether and alcohol in a tube holding 50 c.c., heats the liquid for two hours to 80°, then empties the tube, evaporates down to 10 c.c., agitates the residue with ether, and weighs the residue of the ethereal solution after drying it at 100°.

Brunner (for the analysis of woman's milk) adds acetic acid in quantity sufficient to neutralise the alkaline reaction, heats the liquid to boiling, and adds an indifferent salt, such as magnesium or sodium sulphate. The resulting precipitate contains the whole of the proteïds and of the fat, which latter may be exhausted from it by ether.

J. Horsley (*Chem. News*, xxix. 224) estimates the fat by introducing 15 c.c. of the milk into a graduated glass tube 11 inches long, then adds an equal volume of ether, and agitates continuously for five minutes. An equal quantity of alcohol is then added, and the liquid, after renewed agitation for five minutes, is left at rest for some time, whereupon the fat collects at the top as an oily layer, and may be directly read off by the graduation, or pipetted off and weighed. The casein separated in this operation may be removed by filtration, and the milk-sugar and salts determined in the filtrate by known methods.

E. L. Cleaver (*Pharm. J. Trans.* [3], v. 703, 718) has compared the several methods proposed for the estimation of fat in milk, and has arrived at the following conclusions: (1). Cold ether does not dissolve the whole of the fat from a dry milk-residue. (2). Neither does boiling ether take up the whole if the milk-residue is in the state of a coherent mass. (3). The residue should be finely pulverised, and treated with boiling ether at least 3 or 4 times. (4). During evaporation the boiling of the ether must, as far as possible, be avoided.

* All such additions may, however, be dispensed with, since Wanklyn has shown that milk-residues may be easily and completely dried without the addition of any solid matter (vi. 830).

W. C. Heraeus (*Arch. Pharm.* [3], xii. 443) estimates fat and water in milk by introducing 10 grams of the sample mixed with powdered glass into a small silver boat, placing the boat in an iron tube, one end of which is connected with a Bunsen pump, and the other with a glass tube containing quicklime, and draws air at a temperature of about 35° through the tube for 30 minutes, at the expiration of which time the mixture is found to be perfectly dry. The residue is treated with petroleum ether, and the fat determined from the loss.

Estimation of Nitrogen and Proteïds.—Nencki (*Deut. Chem. Ges. Ber.* viii. 1047) finds the direct method of estimating the proteïds in woman's milk unsatisfactory, and recommends that the milk be evaporated to dryness with lead chromate, and the nitrogen estimated by Dumas' method. The following are the analytical results:

Days after birth	Albumin directly found	Albumin calculated from the nitrogen found
12	1·6	2·26 per cent.
13	1·26	2·26
15	1·25	2·70
4	2·3	3·19
8	1·3	2·40
9	1·12	2·94
10	1·12	1·77
4	1·38	2·75

L. Liebermann (*Wein. Akad. Ber.* [2 Abth.], lxxii. 118) finds that, in the analysis of milk by the methods of Brunner and of Hoppe-Seyler, a considerable portion of the protein-substance escapes precipitation, whereas Haidlen's method precipitates the whole. The proteïds of milk may also be completely precipitated by tannin. Milk contains a proteïd distinct from albumin and casein, but no nitrogenous body not belonging to the proteïd group (comp. Wynter-Blyth, p. 1323).

G. Lachenal (*N. Arch. ph. nat.* lv. 187) has made comparative analyses of the milk of women and of cows, in order to determine whether the whole of the protein-substances can be obtained by precipitation. For cows' milk, he found by precipitation 3·1 per cent., by nitrogen-estimation (Dumas' process) 3·14 per cent. of protein-substance; for woman's milk, 1·41 per cent. by precipitation, 2·53 by nitrogen estimation. For cows' milk, therefore, both methods are applicable, but for woman's milk this is not the case. Cows' milk is richer in proteïds than human milk. The serum of cows' milk, after coagulation of the proteïds, contains neither casein nor albumin, whereas in woman's milk, after coagulation, nearly the half of these bodies remains in the serum.

To estimate the casein, Manetti a. Musso pour 50 c.c. of very slightly acidulated milk into a basin, and heat it to 39°–40° over a water-bath having a temperature of 50°–60°, then add a few drops of glycerin-solution, and expose the liquid to a temperature of 35°–40°. When the coagulation is complete, the mass is chopped up, washed on a filter, and freed from fat by digestion with alcohol and ether, and the coagulum is dried at 115° and weighed. The phosphates precipitated at the same time are estimated by incinerating the dried mass.

The following method for the estimation of casein and fat in milk is given by J. Lehmann (*Liebig's Annalen*, clxxxix. 358–367). Five grams of milk diluted with an equal weight of distilled water are allowed to flow slowly from a pipette on to a porous earthenware plate standing over sulphuric acid, but covered with a clock-glass to prevent the evaporation of the milk. The pores of the plate must be so small as not to admit the passage of the smallest milk-globule, the diameter of which is 0·001 to 0·025 millimeter. In two hours the serum of the milk will be absorbed by the plate, leaving behind the casein and fat. This residue is removed by the aid of a sharp horn spatula, dried for two hours at 105°, and weighed. The fat is dissolved out in the usual way with ether; and the residue, consisting of casein and mineral matter, is weighed, then ignited, and the weight of ash deducted from the weight of casein and ash. This method gives good results; the fat determinations agree with those made by the ordinary process of evaporating to dryness and extracting with ether; but the amount of casein is higher than that which Hoppe-Seyler obtains by precipitating with acetic acid. The great drawback to the process is the difficulty of obtaining plates possessing the requisite degree of porosity.

MILK-SUGAR. See SUGARS.

MINERALS. *Formation of Metalliferous Veins.*—F. Sandberger (*Deut. Chem. Ges. Ber.* x. 2233), has examined a number of rock-forming minerals, such as olivine, hornblende, augite, and mica, for constituents occurring in the metalliferous veins by which the rocks are traversed, e.g. silver, lead, copper, zinc, cobalt, nickel, bismuth,

arsenic. The result of this examination shows a most intimate relation between the minerals in the veins and these traces of constituents in the adjacent rocks, and thus affords a direct proof of Bischof's suggestion 'that the metals of sulphuretted ores existed previously as silicates in the neighbouring rocks.'

Experiments and observations on the accumulation of copper-ores in veins have been published by C. A. Burghardt (*Chem. News*, xxxvi. 281), leading to the conclusion that crystalline rocks contain metallic copper, which is converted by solutions of sodium chloride and carbonic acid into cuprous oxide, cupric chloride, and malachite. Experiment showed further that iron pyrites and a solution of cupric chloride react at 135°-210°, in such a manner as to form cuprous chloride, ferrous sulphate, cupric sulphate, and cuprous oxide; and that cupric chloride with water at 160°-180° yields a body resembling atacamite, together with free hydrochloric acid. The occurrence of brown hæmatite in association with copper ores is referred to the further decomposition of the ferrous sulphate, and the transference of silica to the veins in the form of opal, to the action of the hydrochloric acid on the adjacent rock.

On the Reduction of Noble Metals by Metallic Sulphides in the Veins, see METALS (p. 1287).

Formation of the Minerals which accompany Metalliferous Veins.—Experiments, old and new, on the formation of these minerals, have been published by Th. Scheerer (*Pogg. Ann. Jubelb.* 1874, 314). *Calcspars* is formed from solutions of calcium carbonate in water containing carbonic acid; in like manner *dolomite*, and probably also *brown spar*, from the corresponding solutions. *Barium sulphate* may be obtained in crystals partly grouped together, by heating a dilute solution of barium chloride to 245° with a slight excess of sulphuric acid. The artificial formation of *fluorspar*, and the simultaneous formation of *fluorspar* and *heavy spar*, have already been described in this volume (p. 798). *Silica* and *fluorspar* were obtained by the mutual action of barium silico-fluoride and calcium chloride at 250°, the latter in octohedrons, the former not as quartz but as a hydrate. All Scheerer's experiments on silica led to the same result, so that the attempts to obtain quartz were not successful. The crystallisation of *fluorspar* in octohedrons at high, and in cubes at ordinary temperatures (p. 798), may throw light on the occurrence of the octohedral form in the older veins, and of the cube in those of more recent formation. All these experiments point to the conclusion that the minerals accompanying metallic ores, and therefore also the veins of ore themselves, have been formed in the wet way, in some instances under high pressure and at high temperatures.

Decomposition.—According to F. W. Clarke (*Sill. Am. J.* [3], xiii. 290), many minerals may be decomposed by mixing them in fine powder with a threefold weight of common salt, covering the mixture with 12 to 15 parts of acid potassium sulphate, and fusing it.

Decomposition by Carbonic Acid.—J. R. Müller (*Jahrb. f. Min.* 1877, 739) has examined the action of water containing carbonic acid, continued for seven weeks under a pressure of 3½ atm. on the following minerals and rocks:

1. *Adularia* from the St. Gotthard. 2. *Oligoclase* from Ytterby. 3. *Hornblende rock* from Altenburg: admixed quartz was as far as possible removed. 4. *Magnetic iron oxide* from the Greiner: crystallised. 5. *Magnetic iron ore* from the Kaschberg in Bohemia: a mixture of augite and magnetic iron oxide, which latter was as far as possible removed by the magnet. 6. *Morserite* from Hammond, N. America, in crystals of the combination $\infty P.P.$ $\infty P2$. 7. *Apatite* from Katharinenburg. 8. *Asparagus-stone* (a variety of apatite) from Chili. 9. *Olivine rock* from the Ulten-thal. 10. *Noble Serpentine* from Snarum.

In the following table the first eight columns show the number of parts out of 100 of each constituent of the mineral which passed into solution; the last gives the total amount per cent. of matter produced:

	SiO ^a	Al ¹ O ²	K ² O	Na ² O	MgO	CaO	P ² O ^a	FeO	Total
1.	0.1552	0.1368	1.3627	—	—	trace	—	trace	0.328
2.	0.237	0.1713	trace	2.367	—	3.213	—	trace	0.533
3.	0.419	trace	—	trace	trace	8.528	—	4.829	1.536
4.	—	—	—	—	—	—	—	0.942	0.307
5.	trace	—	—	—	—	29.015	—	2.428	1.821
6.	—	—	—	—	—	1.696	1.417	—	1.529
7.	—	—	—	—	—	2.168	1.822	—	2.018
8.	—	—	—	—	—	1.946	2.12	trace	1.976
9.	0.873	—	—	—	1.291	trace	—	8.733	2.111
10.	0.354	—	—	—	2.649	—	—	1.527	1.211

Former analyses of the several minerals and rocks were used in the calculations,
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so far as they were available; the following analyses were made specially for this inquiry:

	SiO ²	P ² O ⁵	Al ² O ³	Fe ² O ³	FeO	MgO	CaO	K ² O	Na ² O	H ² O	
1.	65.24	—	18.15	—	trace	—	1.28	14.96	—	—	=99.63
3.	49.12	—	9.004	14.62	10.305	5.92	8.761	—	2.13	—	=99.86
5.	1.0655	—	0.4815	61.14	32.2164	—	3.507	—	—	—	=99.4104
6.	—	44.088	—	1.065	—	—	53.319	—	—	—	=98.755
9.	40.60	—	0.86	—	12.35	45.81	trace	—	—	—	=99.62
10.	40.82	—	2.19	—	6.01	36.78	—	—	—	13.48	=99.28

In 6 also Cl=0.283 per cent.; in 9 traces of copper.

The solutions of the following minerals in aqueous carbonic acid were examined only qualitatively: (1). *Potash mica* from the Ural yielded K²O, CaO, Fe²O³, with trace of SiO². (2). *Cobalt-bloom* from Schneeberg, with admixed quartz yielded Co, Ni, Fe²O³, SiO². (3). *Nickel-bloom*: Ni, Co, Fe²O³. (4). *Wolfram* from the Zinnwald, mixed with quartz, MnO, Fe²O³, SiO².

The final conclusions are as follows: Among the silicates examined, the most easily decomposable is olivine; the bases and acids removed from this rock are to one another in about the same proportion as in serpentine. Hornblende is more easily decomposed than felspar; oligoclase more easily than adularia. The most refractory of all the substances was magnetic iron oxide; apatite is easily attacked, and exhibits after treatment a striking contrast to the appearance of the fresh apatite-crystals of the rock under the microscope.

Action of Organic Acids on Minerals.—H. Carrington Bolton (*Chem. News*, xxxv. 114) finds that, contrary to preconceived ideas based on general notions of the weakness of organic acids, many minerals in fine powder are decomposed by boiling with solutions of citric, tartaric, oxalic, and other organic acids. A large number of carbonates dissolve with effervescence in solutions of the above-mentioned acids, and many sulphides, silicates and other classes of minerals are more or less completely decomposed. The reactions which accompany these decompositions, such as evolution of gases, formation of crystalline precipitates, &c., are characteristic of certain minerals. Moreover, since citric and tartaric acids decompose potassium nitrate, with liberation of nitric acid, a powerful means of attacking sulphides and arsenides which resist organic acids alone is obtained. Metallic copper, lead, tin, and silver also dissolve in the above mixture of reagents. Chlorate of potassium is slower in action than the nitrate. Various silicates yield readily to the action of citric acid in solution, gelatinising as with mineral acids. Besides these acids, Bolton also examined the action of malic, formic, and acetic acids on carbonates, for the sake of comparison, acetic acid giving the least satisfactory result. He recommends the use of these non-volatile acids for mineralogical as well as microscopic work, as the dry acids are readily transported, and can be dissolved when needed.

Observations relating to the same subject have been made by B. J. Grosjean (*ibid.* 190), who finds that a weak solution of tartaric acid acts more readily on calcium carbonate than a strong solution containing the same weight of the acid. When the carbonate, either precipitated or in the form of whiting, was digested in 20 pts. of boiling water containing 4 pts. of tartaric acid, nothing was dissolved in either case, even when the acid was doubled and concentrated to a syrup. When, however, the carbonate is treated with 20 parts of water saturated with tartaric acid, the carbonate dissolves even without dilution of the acid.

On the action of *Iodine, Potassium iodide, and Citric acid* on certain Minerals, see Bolton (*Chem. News*, xxxviii. 168; *Chem. Soc. J.* xxxiv. 940).

Pyrometric examinations of individual mineral species have been published by W. A. Ross (*Chem. News*, xxxvi. 106, 156).

On the *Electric Conductivity of Minerals*, see ELECTRICITY (p. 719). On the *Heat-Conductivity of Minerals, Rocks, and Soils*, see HEAT (p. 1017).

On *Fluid-cavities in Minerals*, see p. 793.

Minerals formed by the Volcanic Vapours of Vesuvius.—After the eruption of April 26, 1872, numerous minerals were found amongst the sublimation products, including various silicates and fine crystals of apatite, together with iron pyrites in several forms, and large quantities of tenorite. The crystals of the latter mineral, without losing their shape, have been changed by the hydrochloric acid escaping from the fumaroles, into a green body, named, *ateline* which contains 45.59 of cupric oxide, 38.19 of cuprous chloride, and 16.22 of water. Sylvine and sodium chloride were found in large quantities, and generally mixed together. Sul-ammoniac was abundant and in the finest crystalline forms, but not in octohedrons; it was also found in the fumaroles in beautiful yellow crystals, formed after the colourless ones.

The crystals were black at a spot where a charred tree stump lies buried in the lava. Fluorine was found in combination with ammonia and silica, probably as a double salt, $2\text{NH}_4\text{F} \cdot \text{SiF}_4$, for which the name *cryptohalite* has been proposed. Calcium chloride occurred in large quantities; it seems to have been formed at the beginning of the eruption; cotunnite was abundant. A new mineral, *erythrosiderite*, consists of red rhombic crystals. Ferric chloride, $(\text{Fe}^2\text{Cl}^3 + x\text{H}^2\text{O})$, occurs in the clefts of the lava, and is often mistaken for sulphur. Sodium-potassium sulphate, *aphthalos*, or *aphthitalite*, was found in white hexagonal laminae. Anhydrite was not so common. Hydrofluoric acid was found inside the crater in masses of gypsum and sulphur (G vom Rath, *Jahrb. f. Min.* 1877, 844).

Minerals and Rocks of the Island of Vulcano (A. Cossa, *Gazz. chim. ital.* 1878, 235).—This island, belonging to the Lipari group, contains large deposits of potassium-alum, mixed in various proportions with the alums of thallium, caesium, and rubidium.

The principal deposits of alum are found in the caves of the Faraglione and in the great crater. The Faraglione, also called 'Rocca dell' alume,' is a mass of trachytic rock—decomposed for the most part by sulphuric acid—situated at the southern extremity of the narrow isthmus which joins Vulcanello to Vulcano, and stretching laterally towards the sea. The potassium-alum in its cavities is intimately mixed with aluminium sulphate, gypsum, and sal-ammoniac. In the inner northern wall of the crater of Vulcano there is a rather extensive space called '*la Schicciola*,' formed of a white compact rock to which the potassium-alum adheres in layers of various thickness. From several places in this rock there drips a liquid having a strong acid reaction, and dense enough in some parts to form stalactites with concentric zones. In other parts of the same locality, the liquid which drops from the fissures of the rock contains—in addition to potassium-alum—aluminium sulphate and sodium-alum, which, being much more soluble than the potassium-alum, separate from the latter, and collect at the base of the rock in a crystalline mass of very slender needles, forming the outermost layer of the crystalline matter which adheres to the rock? These more soluble salts exhibit here and there a faint yellow tint due to iron-compounds, or a green tint arising from copper. A specimen examined by the blow-pipe gave the reaction of cobalt, the presence of which was confirmed by testing in the wet way.

The alum of *la Schicciola*, as it comes from the rock, gives a scarcely perceptible indication of the presence of thallium, even when examined with a good spectroscope, the sodium salt with which it is contaminated interfering with the development of the lines which are characteristic of the other metals; but the less soluble salts, when purified by repeated crystallisation, show distinctly, not only the single green line of thallium, but also the lines α and β of caesium and rubidium.

The alum obtained from different parts of *la Schicciola* contains various quantities of caesium and rubidium. The exact amounts have not yet been determined, on account of the difficulty of separating these two metals from potassium, and the still greater difficulty of separating them one from the other. Cossa is, however, of opinion that, with the exception of pollux, a mineral found in extremely small quantities on the island of Elba, the alum of Vulcano is the richest known source of caesium and rubidium.

The separation of caesium from rubidium is most completely effected by Godeffroy's method of precipitation with antimony trichloride from a solution of the two alums in hydrochloric acid, whereby the caesium is completely precipitated in the form of the double chloride, $\text{SbCl}_3 \cdot 6\text{CsCl}$, while the whole of the rubidium remains in solution (*Deut. Chem. Ges. Ber.* vii. 375; viii. 9; *Chem. Soc. J.* 1876, ii. 272). Stollba's method of precipitation with stannic chloride (*Dingl. pol. J.* cxvii. 336; cxviii. 225) does not give good results, the stannochloride of rubidium, as well as that of caesium, being insoluble in strong hydrochloric acid.

To determine whether the rock of *la Schicciola* to which the alum adheres has been simply percolated by a solution of caesiferous alum, or whether the materials of this alum have been furnished by the decomposition of the rock itself, fragments of the rock, after being repeatedly washed with water to remove the alum, were finely pulverised, and the powder was further washed with boiling water, till the washings, when examined by the spectroscope, gave not the slightest indication of potassium. The remaining powder was then decomposed with a mixture of strong sulphuric and hydrofluoric acid, and the mass was washed with boiling water to remove the greater part of the sulphuric acid, whereby a solution was obtained which, when duly concentrated and left at rest, deposited fine crystals of potassium-alum, the solution of which gave by the spectroscope distinct evidence of caesium and rubidium. Hence it is highly probable that these two metals existed in the rock in the form of silicates.

The mother-liquors separated from the first crystals of the alum obtained as just described, and containing large quantities of the sulphates of aluminium and sodium,

with traces of lithium sulphate, yielded, on addition of sulphuric acid, a precipitate of arsenious sulphide mixed with selenium sulphide. The form in which the arsenic and selenium exist in the rock has not yet been determined.

The rock of *la Schicciola* has a white colour with a slight tinge of yellow, and melts with difficulty, even in thin splinters, producing a white enamel. Its sp. gr. at 12° varies from 1·942 to 2·011. It appears to belong to the liparite group, and contains, in the midst of a microfelsitic paste which does not depolarise light, crystals of orthoclastic felspar, some of which are twinned according to the Carlsbad law. The quartz, which is chiefly in the form of tridymite, does not contain any fluid-cavities, but exhibits polyhedral corpuscles. The rock also contains some very small isometric crystals, the mineral species of which has not yet been determined.

Three unaltered lavas from Vulcano, after treatment with sulphuric acid, also yielded crystals of alum containing cesium and rubidium.

On the edges of a small fumarole at the bottom of the crater of Vulcano, there is found a spongy substance having a crystalline texture, reddish on the surface and dark ash-coloured below. It consists of a mixture of arsenious sulphide, selenium sulphide, boric acid, ammonium chloride, lithium sulphate, thallium- and cesium-alums, and traces of rubidium- and potassium-alums. On treating it with boiling water, the sulphides of arsenic and selenium separate out, and the slightly concentrated solution soon deposits the sparingly soluble alums of thallium and cesium.

Another substance, similar to the preceding, except in the absence of the sulphides of arsenic and selenium, is still richer in the alums of cesium and thallium. In all these porous substances which cover the walls of certain fumaroles, and have the aspect of burnt alum, the quantity of cesium is much greater than that of rubidium.

Aluminium sulphate, mixed with traces of alums, occurs also in the numerous mineral springs which rise up in various parts of the island.

To the south-west of the Farglione, not far from the works where the boric acid and sulphur are purified, there is a well containing water about a foot and a half deep, from the bottom of which bubbles of gas are continually rising in large quantity, so as to give the water the appearance of boiling. This gas consists chiefly of carbon dioxide, whence the well was called by C. Sainte-Claire Deville, *la Grotta del Cane dell' isola di Vulcano*. The following are analyses of the gas by Deville and Cossa:

Deville, July 9, 1856. Temp. of the gas + 25°.			Cossa, Oct. 17, 1877. Temp. of the water + 22°.	
CO ₂ .	86·0	83·0	78·0	80·0
O . . .	0·4	0·0	0·5	0·6
N . . .	13·6	17·0	21·5	19·4
	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0

MIRIQUIDITE. This name is given by Frenzel (*Jahrb. f. Min.* 1874, 673) to a blackish or yellowish-brown mineral, accompanying the copper-uranium phosphate (Kupferurangelimner) of Schneeberg in Saxony. It is a highly basic mineral containing Fe²O₃, As²O₃, P²O₅, and H²O. According to vom Rath, the small hexagonal crystals exhibit the combination R. — $\frac{1}{2}$ R, and have the angle R : R = 66°; whence the ratio of the principal to the secondary axes is 3·363 : 1.

MISTLETOE (*Viscum album*). The ash-constituents of this plant, growing on poplar, acacia, and pine, together with those of the wood of these trees, have been analysed by Grandeau and Bouton (*Compt. rend.* lxxxiv. 129, 500). The following table contains the amount of ash per cent. in the dried plants, and the percentage composition of the ash for poplar I, acacia II, and pine III:

These numbers show that the mistletoe assimilates the mineral constituents of the plants on which it lives in very unequal proportions, and that these proportions bear no direct relation to the ash of the plant itself. The amounts of proteids, fat, and woody fibre in the mistletoe likewise vary with those of the plant on which it grows.

Grandeau and Bouton have likewise investigated the proximate composition of the branches, leaves, and fruits of the mistletoe from the oak, willow, dog-wood, and pear-tree, with the view of determining the relative nutritive value of the same when employed for feeding cattle. From the numerical results, the following facts may be gathered:

That while the composition of the leaf and branch of the same specimen is nearly identical, their percentage of nitrogenous constituents, when compared with that of the same parts of mistletoes growing on different trees, varies very greatly, as much as 25·66 to 13·02 per cent. for the leaves, and 20·4 to 7·25 per cent. for the branches.

Ash of Mistletoe.

	Wood			Mistletoe on		
	I	II	III	I	II	III
Ash (free from CO ²)	3·037	2·063	1·609	3·461	2·132	3·139
P ₂ O ₅	4·769	3·453	7·887	26·289	12·025	13·109
SO ₃	1·490	0·784	2·798	2·088	2·741	3·353
SiO ₂	5·813	11·773	2·033	4·791	6·413	1·212
CaO	66·467	75·038	67·429	32·555	45·392	27·133
MgO						12·194
Mn ² O ₃	8·196	2·511	7·124	9·213	6·723	10·670
Fe ² O ₃	2·384	1·884	1·017	5·405	2·198	1·524
K ₂ O	6·557	2·354	8·396	16·093	15·903	30·791
Na ₂ O	2·682	0·471	2·033	2·088	2·585	trace
Cl	1·639	1·726	1·272	1·474	2·017	trace
	99·997	99·994	99·989	99·996	99·997	99·993
Oxygen equivalent to chlorine	0·369	0·388	0·286	0·332	0·482	—
	99·628	99·606	99·703	99·664	99·515	99·993
CO ₂ in 100 pts. of ash	27·47	31·765	25·878	16·636	20·167	18·99

That the fruits of pear-tree and dog-wood mistletoe are comparatively poor in nitrogenous substances.

That the percentage of non-nitrogenous extractive matter varies greatly in mistletoes growing on different trees (53·20 to 39·94 per cent.), while the proportions of gum and resinous matter are tolerably constant.

That the percentage of ash bears no well-marked relation in any way to the nutritive value of the specimen. Grandean a. Bouton are of opinion that the composition of the green parts of the mistletoe, as shown by their analyses, perfectly justifies the use which is made of it in some districts as an article of fodder. They think that the mistletoe of the oak may rank in nutritive value with ordinary grass and clover; that the leaves of the dog-wood and pear-tree mistletoes are about equal to good hay; and that their branches are about equal in nutritive value to pea-straw, bean-straw, and the chaff of cereals.

MOLYBDENUM. *Atomic Weight.*—Rammelsberg, by reducing the trioxide to metal in hydrogen gas, finds for the atomic weight the number 96·18, agreeing nearly with that which Lothar-Meyer found from the analysis of the chlorides (vii. 816), viz. 95·8. Rammelsberg therefore adopts the number 96 (*Ber. x.* 1776).

Estimation.—Wernicke (*Zeitschr. anal. Chem.* 1875, 1) estimates molybdenum volumetrically by reduction with nascent hydrogen (zinc and sulphuric acid) and re-oxidation with permanganate. De-aërated water must be used for dilution, and the titration performed as quickly as possible, since the air acts rapidly on the reduced product. The method is, however, not very exact, the results differing by 1 to 2 per cent.

Alloy. An alloy of molybdenum and lead occurs in plates measuring 30 mm. in the Empire Mine, Lucin District, Box-Elden County, Utah (B. Silliman, *Sill. Am. J.* [3], vi. 128). Hemimorphous crystals of lead molybdiide from the Upper Schwarzgrubner vein at Příbram are described by Zerrenner (*Jahrb. f. Min.* 1874, 91).

Chlorides. The *pentachloride*, MoCl₅, readily parts with two of its chlorine-atoms, and is very useful in the preparation of organic chlorine-compounds as a carrier of chlorine, inasmuch as the molybdenum passes quickly and regularly from one stage of chlorination to another, and is easily removed by ammonia from the product; benzene, for example, is very easily converted by its agency into paradichlorobenzene (p. 172). When carbon disulphide (250 grams) is mixed with the pentachloride (3 or 4 grams), and a strong stream of dry chlorine is passed through the liquid, which must ultimately be warmed, a liquid is formed, which, by fractional distillation and further treatment of the several fractions, may be resolved into carbon tetrachloride and sulphur dichloride, CS₂ + 3Cl₂ = CCl₄ + S₂Cl₂ (Aronheim, *Ber. ix.* 1788).

On the lower Chlorides of Molybdenum, see Liechti a. Kemper (vii. 816).

On the Ferrocyanides of Molybdenum, see CYANIDES (p. 613).

Trioxide, MoO_3 . Molybdic Acid.—When this acid, or either of its salts, is heated with strong sulphuric acid, a mass is formed having a splendid blue colour. On evaporating the sulphuric acid, the residue becomes colourless from oxidation; but on adding fresh acid, the blue colour is reproduced, provided that the substance be removed from the flame after heating for a short time, and left to cool completely. This reaction serves for the detection of very small quantities of molybdic acid; with larger quantities the blue coloration is produced in the cold on addition of a little alcohol or sugar to the sulphuric acid (Schönn, *Zeitschr. anal. Chem.* 1869, 379). O. Maschke (*ibid.* 1873, 380) applies this test by placing a small quantity of strong sulphuric acid on a piece of platinum foil bent up into the form of a trough, then adding a small quantity of the finely pounded substance, heating till vapours are quickly evolved, leaving the whole to cool, and breathing on the foil, whereupon, if molybdic acid is present, the liquid will exhibit a bright blue colour.

Maschke also gives a process for the recovery of molybdic acid from the filtrates obtained in phosphoric acid estimations, depending on the formation of an insoluble compound of molybdic acid with lime and ammonia, and the decomposition of this precipitate by nitric acid. The acid liquids containing molybdenum are poured into jars, and lumps of marble are dissolved in them; the solution, mixed with a slight excess of ammonia, is heated to boiling in an iron pot; and the resulting precipitate, after washing and drying, is drenched with 2 pts. water, mixed, with stirring and gently heating, with 3 pts. nitric acid of sp. gr. 1.18; and the clear solution is heated for some minutes to the boiling point. The precipitate of molybdic acid containing lime and ammonia thereby separated is left to settle, the supernatant liquor still containing molybdic acid, is decanted, and the precipitate is washed by decantation till the liquid begins to clarify but slowly. The moist precipitate is then treated with ammonium carbonate, and the resulting solution of ammonium molybdate is filtered from the calcium carbonate and evaporated over the water-bath. The whole of the wash-waters are united, mixed with ammonia, and heated to boiling, and the calcium molybdate which separates is kept for the next operation.

Uelsmann (*ibid.* 1877, 52) precipitates molybdic acid from the residues with sodium phosphate, washes the precipitate, dissolves it in ammonia, precipitates the resulting solution with magnesia mixture, and evaporates the filtrate. The liquid during evaporation deposits crusts of ammonium molybdate.

Ammonium Molybdate.—Champion a. Pellet (*Bull. Soc. Chim.* [2], xxvii. 6) prepare the molybdenum solution used for precipitation of phosphoric and arsenic acids by dissolving 100 grams of molybdenum trioxide in 150 c.c. ordinary aqueous ammonia and 80 c.c. water, and pouring the solution into a mixture of 500 c.c. nitric acid and 300 c.c. water. If a precipitate forms, it must be filtered off.

According to M. Jungck (*Zeitschr. anal. Chem.* 1876, 290), the yellow crystalline precipitate deposited from a solution of ammonium molybdate—which greatly resembles the well-known precipitate of ammonium phosphomolybdate, but does not contain phosphoric acid—is produced by the action of light, the molybdic acid passing into another modification. He therefore recommends that the solution should be kept in the dark. According to S. Kern, on the other hand (*Chem. News*, xxxvii. 98), this precipitate consists of a basic ammonium salt, and is formed in the dark.

A mixture of the aqueous solutions of ammonium molybdate and potassium ferrocyanide may be used as a test for free mineral acids. Traces of free acids impart to this solution a more or less dark brown colour, which disappears on addition of the slightest excess of alkali (J. Huber, *Zeitschr. anal. Chem.* 1877, 242).

An ammonium molybdate, having the composition $(\text{NH}_4)_2\text{O}(\text{MoO}_3)_3\text{H}_2\text{O}$, is formed, as an amorphous precipitate, by heating a solution of sodium molybdate with sal-ammoniac; and the filtrate mixed with a very large quantity of alcohol, deposits a crystalline mass, which, when dried at 100° , contains 78.70 per cent. MoO_3 , 11.10 NH_3 , and 10.20 H_2O (F. Jean, *Compt. rend.* lxxviii. 1436).

Barium Molybdate has a sp. gr. of 4.6589 at 17.5° , and 4.6483 at 19.5° . **Strontium Molybdate**, 4.1554 at 20.5° , and 4.1348 at 21° (F. O. Marsh, *Sill. Am. J.* [3], xiv. 281).

Silver-diamine Molybdate, $[\text{Ag}(\text{NH}_3)_2]_2\text{O}^2\text{MoO}_2$. See SILVER.

Arseniomolybdates. Ammonium molybdate forms with arsenic acid a compound similar to that with phosphoric acid, and containing $3(\text{NH}_4)_2\text{O}, \text{As}_2\text{O}_5, 20\text{MoO}_3$. When it is boiled with aqua regia and the solutions are evaporated, the residue which is left does not, as in the case of the phospho-compound, consist of the pure acid, but contains in addition insoluble molybdic acid and a second arseniomolybdic acid, which is white. By extracting the residue with dilute nitric acid and evaporating in the desiccator, a mixture of the two acids is obtained in crystals large enough to admit of mechanical separation. The yellow acid forms doubly oblique prisms; its probable

formula is $\text{As}^2\text{O}^3 \cdot 20\text{MoO}^3 + 27\text{H}^2\text{O}$. It gives with acidified potash-salts a yellow crystalline precipitate of $3\text{K}^2\text{O} \cdot \text{As}^2\text{O}^3 \cdot 20\text{MoO}^3$. The hydrated acid corresponding with the phosphomolybdic acid, which crystallises from pure water, has not yet been obtained.

The white arseniomolybdic acid is $\text{As}^2\text{O}^3 \cdot 6\text{MoO}^3 + 16\text{H}^2\text{O}$.⁵ Its ammonium salt may be readily obtained by mixing ammonium molybdate with the theoretical quantity of arsenic acid and crystallising at 50° – 60° . At higher temperatures the yellow salt forms. When the ammonium salt is boiled with aqua regia, a precipitate of yellow arseniomolybdate is at first produced, but subsequently disappears, and the solution on evaporation yields the white acid. It crystallises from syrupy solution in right rhomboidal prisms, and gives white gelatinous precipitates when neutralised with alkalis. The formula of the precipitate with ammonia is $4(\text{NH}^4)^2\text{O} \cdot \text{As}^2\text{O}^3 \cdot 6\text{MoO}^3 + \text{Aq}$ (Debray, *Compt. rend.* lxxviii. 1408).

When a mixture of molybdic acid, arsenic acid, and an ammonium salt is boiled for some time, a crystalline precipitate is obtained, the formula of which is $\text{As}^2\text{Mo}^7\text{O}^{29}\text{H}^6(\text{NH}^3)^2 \cdot 4\text{H}^2\text{O}$. It is soluble in hot water, gives with silver nitrate a yellow precipitate of $\text{As}^2\text{Mo}^7\text{O}^{29}\text{Ag}^+$, and with lead and barium salts precipitates of similar constitution. The acid itself is obtained by the direct combination of arsenic and molybdic acids; its formula is $\text{As}^2\text{Mo}^7\text{O}^{29}\text{H}^6 \cdot 11\text{H}^2\text{O}$. It appears also to be formed on treating the ammonium salt with aqua regia (Seyberth, *Ber.* vii. 391).

Phosphomolybdates. The well-known yellow ammonium salt and the corresponding potassium compound have the composition $3\text{K}^2\text{O} \cdot \text{P}^2\text{O}^5 \cdot 22\text{MoO}^3 \cdot 12\text{Aq}$. By the action of a small quantity of potash-solution, the yellow potassium salt is converted into a white insoluble modification, $5\text{K}^2\text{O} \cdot \text{P}^2\text{O}^5 \cdot 15\text{MoO}^3$. On boiling the alkaline filtrate from this salt, a flocculent precipitate of $\text{K}^2\text{Mo}^6\text{O}^{18}$ is obtained. By dissolving this compound in a small quantity of potash-solution and adding phosphoric acid, a salt is obtained in white shining prisms of the composition $5\text{K}^2\text{O} \cdot 2\text{P}^2\text{O}^5 \cdot 10\text{MoO}^3 \cdot 20\text{Aq}$. By fusing 1 mol. K^2CO^3 with 2MoO^3 , dissolving in water, and adding phosphoric acid to the solution, a compound crystallising in large colourless octohedrons is obtained, the formula of which, $3\text{K}^2\text{O} \cdot \text{P}^2\text{O}^5 \cdot 5\text{MoO}^3 \cdot 7\text{Aq}$, exactly corresponds with that assigned by Zenker (*J. pr. Chem.* lviii. 257) to the colourless compound obtained from the solution of the yellow ammonium phosphomolybdate in ammonia (Rammelsberg, *ibid.* x. 1776).

Sulphides. The native disulphide, *molybdenum-glance*, MoS^2 , occurs, with iron pyrites and copper pyrites, imbedded in greasy quartz, at Macchetto, near Quitergo, in the province of Novara, Piedmont. A and B analyses, C values calculated from the formula MoS^2 :

	A	B	C	Sp. gr.
Mo . . .	58.23	59.05	59.0	4.704
S . . .	41.36	41.17	41.0	
	99.59	100.22	100	

(F. A. Genth, *Jahrb. f. Min.* 1877, 949).

Sulphomolybdate of Ammonium, prepared by treating the bimolybdate with strong sulphuric acid, is a very delicate test for many alkaloïds, especially for *morphine*, with which it produces a distinct blue colour, even to the millionth degree of dilution. The blue colour appears immediately with 1 pt. *morphine* in 100,000 pts. of solution, and in presence of milk-sugar with 3 pts. in 100,000. The blue colour disappears after some hours. *Quinine* gives, with the same reagent, a light green colour which soon disappears; *strychnine*, *atropine*, and *santonine*, no reaction; *veratrine*, a dirty brown colour, changing to blue and finally to yellow-green; *narcotine*, a yellow-green which soon disappears; *brucine* red, changing to yellow. It must be observed, however, that the reagent, even when left to itself, turns blue after a few hours, especially when exposed to light, on which account it must be prepared fresh for use (Nagelvoort, *Arch. Pharm.* [3], ix. 249).

MONAMINES. The synthesis of aromatic monamines by intramolecular atomic interchange—which Hofmann formerly effected in the methyl-series, converting, for example, trimethylphenylammonium iodide, $\text{C}^6\text{H}^3 \cdot \text{N}(\text{CH}^3)^3\text{I}$, by the action of heat, into the hydriodides of the bases $\text{C}^6\text{H}^4(\text{CH}^3) \cdot \text{N}(\text{CH}^3)^2$, $\text{C}^6\text{H}^3(\text{CH}^3)^2 \cdot \text{N}(\text{CH}^3)\text{H}$, and $\text{C}^6\text{H}^2(\text{CH}^3)^3 \cdot \text{NH}^2$ successively (vii. 57)—has, by his later experiments, been extended to aromatic amines containing ethyl and amyl, ethylaniline or ethylamidobenzene, $\text{C}^6\text{H}^4 \cdot \text{NH}(\text{C}^2\text{H}^5)$, for example, being converted by similar means into phenethylamine or amidoethylbenzene, $(\text{C}^6\text{H}^4 \cdot \text{C}^2\text{H}^5) \cdot \text{NH}^2$. See BENZENES, ETHYLAMIDO- and AMYLAMIDO- (pp. 205, 206 of this volume).

MONAS. The spherical Bacterium, called *Monas prodigiosa*, infects eatables, and gives them a red colour. It is conveyed from place to place chiefly by insects, and the spores are also carried through the air. Food placed under a glass shade along with *Monas prodigiosa* turned red in two or three days. When seen under the microscope with a magnifying power of 1000 diameters the monas appears to consist of round bodies, filled with a red substance and swimming in a red fluid.

The colouring matter dyes cotton and linen pink, and wool blood-red; the colour cannot be washed out, but fades on exposure to sunlight. The colouring matter is insoluble in water, and nearly so in ether, but dissolves in alcohol with a blood-red tint; the solution is neutral. There is a marked difference between this dye and the aniline-reds, as shown in the following table:

<i>Aniline-red: a weak solution of Fuch sine.</i>		<i>Colouring-matter of Monas prodigiosa.</i>
Hydrochloric acid	Violet; decolorised by excess.	Pink; unaltered by excess of acid.
Sulphuric acid	Violet; blue with more acid; faint yellow colour with large excess of acid.	Pink; violet with excess of acid.
Nitric acid	No change; with excess first dirty violet, then dull green.	Pink; dirty yellow with large excess of acid.
Potash or ammonia	Colour fades, and is not restored on addition of an acid.	Pure yellow; remains unaltered on heating. On addition of acid the pink colour is restored.
Potassium carbonate	Colour fades.	Yellow.
Ammonium carbonate	No change.	No change.
Stannous chloride	Violet.	No change at first, but gradually bleached.

Lime water, weak solution of chromic acid, and sodium hypochlorite change the yellowish-red colour of the bacterium to yellow; it is destroyed by chloride of lime, or chlorine.

The alcoholic solution of this colouring matter may be kept exposed to light for a long time without change. On evaporation of the alcohol, the colour is obtained in the solid state. It dissolves in petroleum-ether, benzene, and carbon disulphide, in all of which aniline-red is insoluble.

The colour may be obtained tolerably pure by slowly evaporating its alcoholic solution and dissolving the deposit in petroleum-ether, which leaves undissolved a brown tarry residue. On evaporation of the solution in petroleum-ether, the dye is obtained in the same state (O. Helm, *Arch. Pharm.* [3], vi. 19).

MONAZITE. Native Cerium Phosphate. See PHOSPHATES.

MONOTHIODIPRUSSIAMIC ACID. See THIOPRUSSIAMIC ACIDS.

MONTICELLITE, or *Batrachite*. Two analyses of this mineral from Monte Monzoni, leading to the formula $\text{Ca}^2\text{SiO}^4(\text{Mg},\text{Fe})^2\text{SiO}^4$, have been published by G. vom Rath (*Zeitschr. geol. Ges.* xxvii. 379):

SiO^2	FeO	CaO	MgO	Total	Loss by ignition	Sp. gr.
38.35	4.29	34.76	23.15	= 100.55	1.31	3.054
38.15	4.31	34.75	22.94	= 100.15		

MONZONITE. This name, originally applied by v. Kobell to a mineral species from Monte Monzoni (vii. 818), has also been given to a rock from Monte Agnello, South Tyrol, consisting of plagioclase, orthoclase, hornblende, augite, mica, and magnetic iron ore. This rock has a porphyritic structure like that of melaphyre. Its percentage composition is as follows:

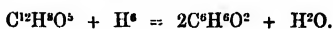
SiO^2	Al^2O^3	Fe^2O^3	MnO	CaO	MgO	K^2O	Na^2O	Loss by ignition
52.53	19.48	11.07	trace	6.61.	1.53	3.17	2.71	2.34 = 99.44

(Dölter a. Mattendorf, *Ver. geol. Reichsanst.* 1876, 33). According to C. W. Gumbel, v. Kobell's monzonite is not a homogeneous mineral.

MOONSTONE. This name has been applied to a monoclinic felspar from Ceylon, a variety of *adularia* (ii. 620); also to a triclinic felspar from Mineral Hill,

Delaware County, Pennsylvania, regarded by Dana (*System of Mineralogy*, 5th Ed. p. 348) as a variety of oligoclase; according to Des Cloizeaux (*Comp. rend.* lxxx. 364), it is a variety of albite.

MORIN, $C^{15}H^{10}O^7$. This compound has hitherto been known in two modifications, viz. *Morin* and *Isomorin* (vi. 837). A third, called *Paramorin*, is obtained, together with resorcin, by the distillation of morin. When morin in portions of 1 to 2 grams is mixed with 4 or 5 parts of sand and distilled, a distillate is obtained, amounting, after expulsion of water, to 25 per cent. of the morin. After recrystallising the product from hot water, the resorcin may be extracted from the mother-liquor by ether, and the paramorin, $C^{12}H^8O^5$, crystallises from the solution on cooling in long, foliated, slightly yellow, woolly, anhydrous needles, which may be purified by recrystallisation with addition of blood-charcoal. It is tasteless; melts when heated, and sublimates without decomposition; reduces an alkaline cupric solution; colours ferric chloride but slightly, and dissolves in sulphuric acid without change of colour. Paramorin dissolves very easily in boiling water and in ether (morin is but slightly soluble in these liquids, iii. 1048), and with deep yellow colour in alkalis. From its alcoholic solution, alcoholic lead acetate throws down only small quantities of a lead salt (whereby it is distinguished from morin). With nitrous acid it forms a yellow nitro-derivative; with sodium-amalgam, resorcin or a diresorcin:



The quantity of paramorin obtained in the distillation of morin is but small, the chief product consisting of resorcin. The woolly crystals with which morin becomes covered when heated consist of undecomposed morin (Benedikt, *Ber.* viii. 605).

Respecting Löwe's formulæ for Morin and Morintannic acid, see MACLURIN, (p. 1244).

MORINGIC ACID. This name was given by Walter to an oily acid obtained by saponification of oil of ben (*Moringa aptera*), and regarded by him as a lower homologue ($C^{13}H^{20}O^2$) of oleic acid (iii. 1049). Zaleski, however (*Deut. Chem. Ges. Ber.* vii. 1013), finds, by an examination of a sample of the acid prepared by Walter himself, that it is identical with oleic acid. The identity was shown by conversion of the acid by means of nitrous acid into elaidic acid (m. p. 49°); by its conversion into the oleic dibromide, $C^{18}H^{34}Br^2O^2$, prepared by Overbeck from oleic acid (vi. 881), and transformation of the latter into stearolic acid [m. p. 48° ; formula of barium salt ($C^{18}H^{31}O^2$) 2Ba , vi. 1038], and finally by fusion with potash, whereby, like oleic acid, it yielded palmitic and acetic acids.

MORINTANNIC ACID. See MACLURIN (p. 1244).

MOROXITE. A greenish-blue variety of apatite, originally found at Arendal in Norway, and Pargas in Finland, has lately been found at Hammond, North America, in crystals exhibiting the combination $\infty P.P.\infty P_2$, and containing 44.09 per cent. P_2O_5 , 53.32 CaO, and 1.065 Fe_2O_3 (J. R. Müller, *Jahrb. f. Min.* 1877, 739).

MORPHINE, $C^{17}H^{13}N^2O^6$. *Solubility.*—The solubility of morphine in various solvents saturated with water, and at the boiling heat, has been determined by A. B. Prescott (*Pharm. J. Trans.* [3], vi. 404) with the following results:

Morphine	Ether	Chloroform	Amyl Alcohol	Benzene
Crystallised	6148 parts	4379 parts	91 parts	8930 parts
Amorphous	2112 "	1977 "	—	—
Nascent	1062 "	861 "	91 "	1997 "

According to J. B. Barnes (*ibid.* 201) the solution of morphine in glacial acetic acid forms a perfectly clear mixture with almond-oil and turpentine-oil. The solution remains clear and unaltered for several days if mixed with chloroform or camphor, and may be prepared of any required degree of concentration.

Reactions. Detection.—1. With ammonium sulphomolybdate, morphine gives a blue colour, perceptible to the millionth degree of dilution (p. 1334). 2. With hydrogen sulphide, see ALKALOIDS (p. 56). 3. With iodised hydriodic acid, see p. 55. 4. An ammoniacal solution of copper is a delicate test for morphine, losing its splendid colour when boiled therewith, and acquiring a distinct green-blue tint. The copper solution is to be added by drops to a clear and strongly alkaline solution of morphine, till a light blue colour is produced, and the liquid then boiled up once or twice. This test will detect with certainty 1 mg. morphine to the thousandth degree of dilution. The presence of other alkaloids does not interfere with the reaction (G. Nadler, *Zeitschr. anal. Chem.* 1874, 235).

Nadler also describes a base obtained (he does not say how) by treating morphine with an ammoniacal cupric solution. The hydrochloride of this new base is described

as a dazzling white substance insoluble in cold, easily soluble in hot water, insoluble in alcohol and ether. Its aqueous solution, treated with ammonia or potassium carbonate, yields the base as a dense white amorphous precipitate, which dissolves in excess of the precipitant at ordinary temperatures, but may be recovered by boiling the potash-solution, and dries up without alteration on exposure to the air, like aluminium hydrate. The aqueous solution of the hydrochloride gives a pale yellow precipitate with platonic chloride, white amorphous with sulphuric acid, and amethyst-red with ferric chloride. Sulphuric acid with the aid of heat dissolves the base, forming a black-green liquid, which may be heated without alteration till the acid volatilises.

5. Another test for morphine is based upon the reaction of *sulphomorphide with ammonia*, which forms with it a precipitate soon becoming reddish-brown, and dissolving with rose-red colour on agitation with chloroform. Sulphomorphide is easily formed by heating morphine to 150° with a mixture of 2 vols. sulphuric acid and 1 pt. water (Nadler, *loc. cit.*)

6. The presence of morphine may also be detected by adding a few drops of strong sulphuric acid to the substance under examination, and then a small granule of *potassium perchlorate*, which must be quite free from chlorate; if morphine is present, the liquid will assume a dark-brown colour (Grove, *Zeitschr. anal. Chem.* 1874, 324; Siebold, *ibid.*)

7. For the detection of morphine in chemico-legal investigations, Selmi (*Gazz. chim. ital.* 1875, 255) recommends the use of iodised hydriodic acid followed by tetracetate of lead (comp. p. 55).

On Dragendorff's Method of detecting Morphine in a mixture of Alkaloids, see PLANT-BASES.

On the Action of Organic Acids upon Morphine, see DERIVATIVES (p. 1341).

Certain oxidising agents, viz. *nitric acid, iodic acid, potassium ferricyanide, potassium chromate*, and the *dioxides of manganese and lead*, produced in acidulated solutions of morphine, on gentle heating, a deep red colour, even when the quantity of morphine is very small. The best way of applying the test is to add to the substance under examination, first sulphuric acid, then water, and lastly the oxidising agent, if possible in the solid state. The best result is given by iodic acid (D. Lindo, *Chem. News*, xxxvi. 228). D. Datt (*ibid.* 255) observes that this reaction, at least with nitric acid and with potassium dichromate, is produced also by salts of codeine and narcotine, but not by thebaine, papaverine, or narcine. To detect the presence of morphine in quinine salts, H. Hager (*Zeitschr. anal. Chem.* 1873, 220) makes use of Kieffer's reaction (*Liebig's Annalen*, ciii. 271), which consists in adding to the solution a mixture of potassium ferricyanide and ferric chloride acidulated with hydrochloric acid, the ferricyanide being then reduced by the morphine to ferrocyanide, which, with the ferric chloride, produces prussian blue.

Estimation.—For the estimation of morphine in opium, C. Arnoldi (*Russ. Zeitschr. Pharm.* 1873, 611) exhausts the opium completely with water, which should not leave more than two-thirds undissolved; concentrates the aqueous solution on the water-bath; filters it when cold; decolorises it with animal charcoal, and filters again; precipitates the morphine with ammonia, and weighs it. Good opium thus treated should yield from 14 to 19 per cent. of impure morphine, answering to 10 to 13½ per cent. of the pure base.

See also J. Lynn (*Amer. J. Pharm.* [4], vi. 358; *Chem. Centr.* 1878, 158; *Chem. Soc. J.* xxxiv. 612).

SALTS OF MORPHINE. The solution of the *acetate* has a strong tendency to deposit a basic salt or free morphine; the salt decomposes and turns yellow even when kept in carefully closed vessels, and then gives with sulphuric acid no longer a colourless but a yellow solution.

The *hydriodide*, $C^{17}H^{19}NO^3.HI + 2H^2O$, obtained either by saturation or by the action of potassium iodide on morphine acetate, crystallises in long silky needles grouped in rosettes, sparingly soluble in cold water (insoluble according to Bauer, *infra*), more freely in hot water. The water of crystallisation is given off at 100° , and reabsorbed on exposure to the air (E. Schmidt, *Ber.* 1877, 194; *comp.* Winkler, iii. 1054).

The *hydrobromide*, $C^{17}H^{19}NO^3.HBr + 2H^2O$, is very much like the hydriodide (Schmidt).

Periodides. The *sesqui-iodide*, $2C^{17}H^{19}NO^3.I^2$, prepared by triturating 2 pts. morphine with 1 pt. iodine, and crystallising the mixture from alcohol, is a reddish-brown crystalline mass, soluble in alcohol, ether, and chloroform, but insoluble in water. The *tetrioide*, $C^{17}H^{19}NO^3.HI^4$, is obtained by precipitating a morphine salt with iodine-solution, as a kermes-brown precipitate, which dissolves in potassium

iodide, and crystallises therefrom in long nearly black prisms, insoluble in ether and in carbon sulphide, soluble in alcohol, benzene, and chloroform. Nitric acid and hydrochloric acid dissolve it with red colour (H. R. Bauer, *Arch. Pharm.* [3], v. 289).

Substitution-derivatives of Morphine.

Acetyl-derivatives. Mono-, di-, and tetracetyl-morphine have been already described (vii. 819, 820). Further observations on the diacetyl-derivatives have been published by Beckett a. Wright (*Chem. Soc. J.* xxviii. 315), who have obtained a third modification (γ) in crystals by dissolving the β -modification in ether, and leaving the solution to evaporate. The mother-liquor then retains a portion of the β -compound unmixed with any other modification. The β -compound appears to give a blue colour with ferric chloride, only when it is decomposed or perhaps contaminated with mono-acetyl-morphine, inasmuch as the production of this colour-reaction, though usual, is not constant.

The following table gives a comparative view of the properties of the three diacetyl-morphines.

	Relative Quantity.	Properties of		
		Free Base.	Hydrochloride.	Ethiodide.
α -Diacetyl-morphine.	2 to 3 per cent.	Crystallises from ether by spontaneous evaporation, sometimes anhydrous, sometimes with 2 mols. water.	Proportionally less soluble in cold water. Crystals contain $6H^2O$.	Crystallises from alcohol of 85 per cent. with 1 mol. water.
β -Diacetyl-morphine.	Forms the chief product.	Quite uncrystallisable.	Very soluble, amorphous; in aqueous solution much less stable than its isomerides.	Does not crystallise from alcohol of 85 per cent. or from absolute alcohol.
γ -Diacetyl-morphine.	25 per cent.	Crystallises readily, anhydrous, if free from β -compound.	Very soluble in water; crystallises with difficulty.	Crystallises from alcohol of 85 per cent. with 3 mols. water.

Butyryl-morphines (Beckett a. Wright, *Chem. Soc. J.* xxviii. 16). *α -Dibutyryl-morphine*, $C^{11}H^{18}(C^4H^7O)^2N^2O^6$, formed by boiling morphine for five or six hours with twice its weight of butyric acid, crystallises readily from ether, and when pure does not give any colour-reaction with ferric chloride. Its *hydrochloride* is more soluble and crystallisable than that of the corresponding acetyl-base. The ethereal mother-liquor contains β -dibutyryl-morphine, an amorphous base which gives a blue colour with ferric chloride. *Tetrabutryl-morphine*, formed by heating morphine to 140° for three hours with twice its weight of butyric anhydride, is amorphous, and is very slowly resolved by boiling with water, somewhat more readily with dilute alcohol, into butyric acid and dibutyryl-morphine. Its *hydrochloride*, $C^{11}H^{14}(C^4H^7O)^4N^2O^6 \cdot 2HCl$, is also amorphous, and does not give a blue colour with ferric chloride. *Acetyl-butyryl-morphine* was formed by boiling morphine for several hours with a mixture of acetic and butyric acids, in which the former greatly predominated. Its *hydrochloride*, $C^{11}H^{18}(C^2H^3O)(C^4H^7O)N^2O^6 \cdot 2HCl$, is crystalline, and is very easily resolved, by boiling with water, into the hydrochlorides of diacetyl- and dibutyryl-morphine.

Benzoyl-morphines (Beckett a. Wright, *Chem. Soc. J.* xxviii. 23). *Dibenzoyl-morphine*, $C^{11}H^{16}(C^7H^5O)^2N^2O^6$, is formed by the action of benzoic anhydride on morphine; also, together with benzoic acid, by boiling a solution of tetrabenzoyl-morphine in dilute alcohol. The base thus obtained is amorphous; its hydrochloride is crystallisable, very slightly soluble in water, and is not altered by ferric chloride.

α -Diacetyl-dibenzoyl-morphine, $C^{11}H^{14}(C^7H^5O)^2(C^4H^7O)^2N^2O^6$, formed by the action of benzoic anhydride on α -diacetyl-morphine, is a crystalline base. Its *hydro-*

chloride is very soluble in water, does not crystallise, and is precipitated in flocks by strong nitric acid.

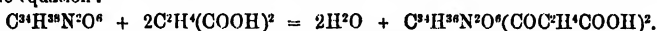
Tetrabenzoyl-morphine, $C^{24}H^{24}(C^6H^5O)^4N^2O^6$, is prepared by heating morphine to about 130° for three or four hours with twice its weight of benzoic anhydride. On dissolving the product in hot dilute hydrochloric acid, precipitating with sodium carbonate, dissolving the precipitate in ether, and leaving the ether to evaporate, the base separates in anhydrous crystals which give no colour-reaction with ferric chloride. Its *hydrochloride*, $C^{24}H^{24}(C^6H^5O)^4N^2O^6 \cdot 2HCl$, is amorphous, but in other respects resembles that of dibenzoyl-codeine (p. 1341).

Ethioidides of Substituted Morphines (Beckett a. Wright, *Chem. Soc. J.* xxviii. 318). These compounds are formed by heating the respective bases to 100° for about a quarter of an hour with twice their weight of absolute alcohol and about an equal weight of ethyl iodide. The contents of the tubes usually solidify on cooling, in crystals which may be recrystallised from alcohol of 80–85 per cent.

Tetracetyl-morphine Ethioidide is a somewhat unstable compound, a considerable portion of it being decomposed by a few minutes' boiling with alcohol of 85 per cent. The crystals deposited from this solvent contain $C^{24}H^{24}(C^2H^3O)^4N^2O^6 \cdot 2C^2H^3I + H^2O$, and the mother-liquor contains products apparently resulting from removal of acetyl by the alcohol. Silver chloride converts the ethioidide into the corresponding ethylchloride, which is readily soluble, but cannot be obtained in the pure state, as the aqueous solution decomposes partially when heated, or when left over sulphuric acid.

α -*Diacetyl-morphine Ethioidide*, and the isomeric γ -compound, crystallise, the first with 1 mol., the second with 3 mols. H^2O ; the β -compound is amorphous, as are also the ethioidides of dibutyl- and tetrabutyl-morphine, which decompose at 100° . The ethioidides of tetrabenzoyl- and diacetyl-dibenzoylmorphine crystallise with 1 mol. water.

Morphine-derivatives containing Polyatomic Acid Radicles (Beckett a. Wright, *Chem. Soc. J.* xxviii. 689). These compounds are formed by heating morphine with polybasic acids. Morphine, heated to 180° with twice its weight of *succinic acid*, yields the compound $C^{24}H^{24}N^2O^6(COC^2H^4COOH)^2 + 8H^2O$, which closely resembles the corresponding codeine-compound (p. 1341). Its formation is represented by the equation:



With camphoric acid in like manner, morphine yields a small quantity of the compound, $C^{24}H^{24}N^2O^6(O.CO.C^6H^4(COOH)^2$.

With *oxalic acid*, morphine reacts like codeine (p. 1342), not forming an oxalyl-morphine, but yielding a product consisting chiefly of trimorphine.

Appendix to Morphine.

Alkaloid resembling Morphine (Selmi, *Gazz. chim. ital.* 1875. 398). The detection of small quantities of morphine in the brain and liver is very much interfered with by the presence of another alkaloid very closely resembling it. This base in aqueous solution exhibits an alkaline reaction; it is insoluble in ether, but dissolves in amyl alcohol; reduces iodic acid; is coloured bluish by ferric chloride; does not exert any poisonous action on frogs.

A base very similar to this, and perhaps identical with it, is found in the unripe capsules of the wild poppy. It is distinguished from morphine by the following reactions. Morphine gives with *iodised hydriodic acid* microscopic crystals, which take a considerable time to form, but then remain permanent for 36 hours; the new base, on the other hand, yields crystals which form immediately but quickly disappear. When a drop of dilute morphine solution mixed with a drop of a cold-prepared solution of *minium* in *glacial acetic acid* is evaporated at a gentle heat, there remains a yellow residue, the colour of which changes through orange to violet, and finally becomes dull and indistinct. The new base similarly treated yields an unalterable yellow residue.

Codeine, $C^{26}H^{42}N^2O^6$. Crystals of codeine, which Flückiger obtained by crystallising the base dried at 100° from carbon sulphide, have been examined by Arzruni (*Zeitschr. Kryst.* i. 302). They are yellowish by transmitted light, strongly refractive, and belong to the orthorhombic system with hemihedro-sphenohedral development, $a : b : c = 0.9298 : 1 : 0.5087$. Plane of optic axes OP.

Acetyl-, Butyl-, and Benzoyl-codeines (Beckett a. Wright, *Chem. Soc. J.* xxviii. 212). *Diacetyl-codeine*, formed by boiling codeine with twice its weight of glacial acetic acid, has been already described (vii. 821).

Tetracetyl-dicodeine, $C^{52}H^{70}(C^2H^3O)^4N^2O^{12}$, obtained by the action of acetic anhydride on dicodeine (vii. 735), is amorphous, easily soluble in ether, and forms a

crystallisable *hydrochloride*, $C^{72}H^{80}(C^2H^3O)^4N^4O^{12}.4HCl + 10H^2O$, more soluble than the hydrochloride of diacetyl-codeine, and an indistinctly crystallised *platinochloride*, $C^{72}H^{80}(C^2H^3O)^4N^4O^{12}.4HCl.2PtCl^4$.

Octacetyl-tetracodeine, $C^{144}H^{160}(C^2H^3O)^8N^4O^{24}$, is obtained by heating tetracodeine with acetic anhydride to 120° for three hours, and evaporating the product to dryness, as a mass insoluble in water and dilute hydrochloric acid, soluble in alcohol and alcoholic hydrochloric acid, and precipitated from these solutions by water in amorphous flocks which become darker when dried over sulphuric acid. The solution in alcoholic hydrochloric acid mixed with alcoholic platinum tetrachloride and then precipitated with water, yields a basic *platinum salt*, the amount of platinum in which agrees approximately with the formula $C^{144}H^{160}(C^2H^3O)^8N^4O^{24}.2HCl.PtCl^4$.

In the conversion of codeine into di- and tetracodeine, the number of hydroxyl-groups in the molecule is not diminished, and the polymerised bases are capable of yielding neutral salts, but their acetyl-derivatives are not.

ETHIODIDES. *Diacetyl-codeine Ethiodide*, $C^{36}H^{40}(C^2H^3O)^2N^2O^6.2C^2H^5I + H^2O$, is obtained by heating codeine with twice its weight of absolute alcohol and about an equal weight of ethyl iodide, to 100° for about a quarter of an hour. It forms snow-white crystals, slightly soluble in cold alcohol either absolute or of 90 per cent., more easily in water and in hot dilute alcohol. It gives off its water at 100° , being at the same time partly decomposed. By the action of recently precipitated silver chloride and water, it is converted into *diacetyl-codeine ethylchloride*, which separates on leaving the solution over sulphuric acid, in crystalline crusts having, when dried at 100° , the composition $C^{36}H^{40}(C^2H^3O)^2N^2O^6.2C^2H^5Cl + H^2O$. The *platinochloride* decomposes in drying.

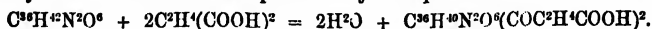
When *tetracodeine* is heated for twenty minutes in a sealed tube to 120° with an equal weight of ethyl iodide, and the resulting liquid is left to cool, amorphous flocks are deposited which dissolve in boiling alcohol and in hot water, and have the composition $C^{144}H^{160}N^4O^{24}.8C^2H^5I$. *Octacetyl-tetracodeine*, treated in like manner, yields a much more soluble compound, containing 12.72 per cent. iodine, whereas the formula $C^{144}H^{160}(C^2H^3O)^8N^4O^{24}.8C^2H^5I$ would require 25.55 per cent. iodine, and the corresponding formula with $4C^2H^5I$ would require 15.15 per cent. Hence it would appear that the power of a polymeric codeine to take up ethyl iodide is diminished when it is converted into an acetyl-derivative.

Dibutyl-ryl-codeine, $C^{36}H^{40}(C^4H^7O)^2N^2O^6$, is formed by boiling codeine for five or six hours with twice its weight of butyric acid, and by evaporating off the excess of acid, dissolving the residue in water, precipitating with sodium carbonate, dissolving the precipitate in dilute hydrochloric acid, reprecipitating, and finally dissolving the precipitate in ether and leaving the ether to evaporate, it may be obtained as an amorphous perfectly uncrystallisable mass. It is also produced by the action of butyric anhydride on codeine. Its *hydrochloride*, $C^{36}H^{40}(C^4H^7O)^2N^2O^6.2HCl + 6H^2O$, crystallises well, gives off its water of crystallisation at 100° , and yields a *platinochloride* having the composition $C^{36}H^{40}(C^4H^7O)^2N^2O^6.2HCl.PtCl^4$.

Dibenzoyl-codeine, $C^{36}H^{40}(C^7H^5O)^2N^2O^6$, formed by the action of benzoic anhydride on codeine, crystallises anhydrous from ether. It dissolves but very sparingly in water either cold or hot, and is not altered by boiling with water. Its hydrochloride forms, with a large quantity of warm water, a clear solution, which on cooling becomes opalescent like starch-paste; and if the solution was concentrated it deposits a soft amorphous mass which may be crystallised, and has the composition $C^{36}H^{40}(C^7H^5O)^2N^2O^6.2HCl + 2H^2O$. The *platinochloride* is anhydrous and more soluble in alcohol than in water.

The *ethiodides* of dibutyl- and dibenzoyl-codeine crystallise with 1 mol. water.

Codeine-derivatives containing Polyatomic Acid Radicles (Beckett & Wright, *Chem. Soc. J.* xxviii. 689). *Succino-codeine* or *Codeine-succinic acid*, $C^{36}H^{40}N^2O^6(COC^2H^4COOH)^2$, is formed by heating codeine to 180° with twice its weight of succinic acid, whereupon the whole becomes liquid; and on dissolving the product in water, and freeing it by fractional precipitation with sodium carbonate or ammonia from coloured impurities which separate out first, and then cautiously adding further quantities of the precipitant, the pure compound is thrown down in white flocks, and on dissolving those in boiling alcohol, the acid separates on cooling in small crystals. Its formation is represented by the equation:



The crystals, when air-dried, contain 10 mol. H^2O , which they give off at 100° . The acid is insoluble in water, ether, and benzene, slightly soluble in cold, easily in boiling alcohol, also in acids and in excess of alkali. Its alkali-salts could not be prepared. Its solution in baryta-water is decomposed by carbonic acid; an ammoniacal solution

evaporated over sulphuric acid leaves the acid unaltered, and the addition of silver nitrate is followed by separation of metallic silver.

The compounds with acids, on the other hand, are easily prepared. A solution in hydrochloric acid yields, when evaporated over oil of vitriol, crystals of the compound $C^{14}H^{50}N^2O^{12} \cdot 2HCl + 2H^2O$, which gives off its water at 100° , and yields a flocculent precipitate with platinic chloride.

The compound $C^{36}H^{40}N^2O^6(COC^2H^4COOH)^2$ is analogous in constitution to Lourenço's succinethylenic acid, $C^4H^4O^2 \left\{ \begin{smallmatrix} C^2H^4 \\ H^2 \end{smallmatrix} \right\} O^3$ (ii. 582), which, however, more readily forms metallic salts, but is incapable of uniting with other acids.

Camphoro-codeine, or Codeine-camphoric acid, $C^{36}H^{40}N^2O^6(C^{10}H^{13}O^3)^2$.—Camphoric acid and codeine, heated together, form a hard mass, from which may be extracted a crystalline body having the composition above given. It crystallises from dilute alcohol with 8 mol., from alcohol of 80 per cent. with 6 mol. H^2O ; forms a hydrochloride which is slightly soluble in cold water, crystallises from dilute alcohol, has when air-dried the composition $C^{56}H^{70}N^2O^{12} \cdot 2ClH + 2H^2O$, and forms an amorphous platinochloride.

Tartaric acid and **Codeine** yield, when heated together, a solid mass, the greater part of which dissolves in water. The residue is insoluble in aqueous but soluble in alcoholic hydrochloric acid, and is reprecipitated by water and alkalis, in the latter case free from chlorine. The hydrochloride and platinochloride contain much less chlorine than might be expected from analogy to the derivatives above described. The product of the reaction may perhaps be regarded as a tartrato-derivative of tetra-codeine, which, like acetyl-tetracodeine, has lost some of its binding power.

Oxalic acid and codeine, heated together, melt to a clear liquid, which gives off large quantities of carbon dioxide and monoxide in about equal volumes, and afterwards acid vapours. The oxalyl-derivative could not be isolated, but the product contained di-codeine and probably also tri- and tetra-codeine. Beckett a. Wright are of opinion that these polycodeines are produced from a very easily decomposable codeine-oxalic acid formed in the first instance, and that the formation of the same polymerides by the action of sulphuric and phosphoric acids on codeine (vi. 481; vii. 372) is in like manner preceded by that of intermediate compounds which cannot be isolated.

MOSANDRIUM. See YTTRIUM-METALS.

MOTTRAMITE. See VANADATES.

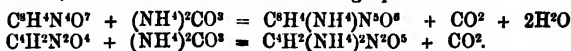
MUCIC ACID, $C^8H^{10}O^8$. This acid, treated with phosphorus pentachloride, yields a chloride convertible by water into chloromuconic acid, $C^8H^4Cl^2O^4$, which, when treated with water and sodium-amalgam, yields hydromuconic acid, $C^8H^8O^4$; and this latter, dissolved in glacial acetic acid and treated with bromine, yields isodibrom-adipic acid, $C^8H^8Br^2O^4$, which is converted by silver oxide into the silver salt of muconic acid, $C^8H^2O^4$ (vii. 827).

MUCOBROMIC ACID, $C^8H^2Br^2O^4$, is formed by adding bromine in excess to pyromucic acid dissolved in water (vii. 828).

MUCOR. On Alcoholic Fermentation produced by *Mucor Mucedo* and *Mucor racemosus*, see vii. 518; viii. 776. According to Müntz (*Compt. rend.* lxxix. 1182), *Mucor Mucedo* contains trehalose.

MUREX. According to A. and G. de Negri, the purple of *Murex trecuculus* consists of two colouring matters, one of which is identical with indigo-blue. The juice of *Murex trecuculus* becomes coloured on exposure to the air, even in the dark; that of *Murex brandaris* only in the light.

MUREXAN and MUREXID. According to Magnier de la Source (*Bull. Soc. Chim.* [2], xxii. 56), the so-called murexid reaction is to be ascribed partly to the formation of ammonium isalloxanate, $C^4H^4(NH^4)^2N^2O^5$, partly to that of acid ammonium purpurate, $C^6H^4(NH^4)^2N^2O^6$. The latter compound is formed from alloxantin by the action of ammonium carbonate, while alloxan, treated with the same reagent, yields the former, as will be seen from the following equations:



Consequently, a mixture of alloxan and alloxantin, treated with ammonium carbonate, will produce both these colouring matters. The ammonium isalloxanate may be partly removed from the mixture by washing, and partly remains, perhaps with the purpurate, a circumstance which sufficiently accounts for the great differences among chemists respecting the formula of murexid. See also J. Resch (*Chem. News*, xxxii. 171)

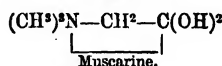
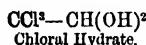
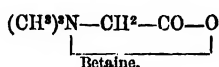
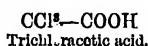
MURRAYIN, $C^{16}H^{22}O^{10}$. A glucoside from the flowers of *Muraya exotica*, m. p. 245° (De Vrij, *Jahresb. f. Chem.* 1876, 850).

MUSA. The colouring matter of *Musa Fehii*, a tree growing on the highlands of Tahiti, is described by Niederstadt (*Dingl. pol. J.* cexix. 165). The juice separates into a caoutchouc-like mass, and a watery liquid having a raspberry colour in thin, blue-violet in thicker layers. This liquid dyes cotton and linen greyish-violet with alum-mordants, and a splendid violet with tin-mordants.

MUSCARINE, $C^5H^{13}NO^2$. An alkaloid occurring, together with amanitine (choline), in the fly-agaric (*Agaricus muscarius*). The mode of separating the two has been already described (p. 456). Muscarine may be formed artificially by gently heating choline hydrochloride or platinochloride with strong nitric acid; its sparingly soluble platinum salt is easily separated from undecomposed choline platinochloride. The platinochloride of muscarine, decomposed by potassium chloride, yields muscarine hydrochloride, $C^5H^{13}NO^2.HCl$, which is converted by moist silver oxide into the hydrate $C^5H^{13}NO^2.H^2O$, or hydroxide, $C^5H^{14}NO^2.OH$, agreeing in all its properties with the base obtained from the fly-agaric.

Muscarine hydroxide forms irregular deliquescent crystals having an alkaline reaction; it forms an alkaline salt with carbonic acid, neutral salts with the stronger acids. The aurochloride has the composition $C^5H^{14}NO^2.Cl.AuCl^3$; the platinochloride is $(C^5H^{14}NO^2.Cl)^2PtCl^4 + 2H^2O$.

Muscarine is related to betaine in the same manner as chloral hydrate to trichloroacetic acid:



Muscarine hydroxide is represented by the formula $(CH^3)^3N \begin{smallmatrix} OH \\ \diagdown \\ CH^2-CH(OH)^2 \end{smallmatrix}$ (Schmiedeberg a. Harnack, *Chem. Centr.* 1876, 554).

MUSCOVITE. See MICA (p. 1319). A description of the localities of Bengal muscovite is given by O. Feistmantel (*Verh. geol. Reichsanst.* 1875, 301; *Jahresb. f. Chem.* 1875, 1219).

MUST. See WINE.

MUSTARD. *Detection of Adulterations*.—Wheat-flour, &c., may be easily detected by the formation of iodide of starch on addition of iodine-tincture; turmeric by its appearance under the microscope, by the borax reaction, and by the fluorescent properties of its alcoholic solution (see TURMERIC); gamboge by the reddening which it exhibits with alkalis; Cayenne pepper also by the microscope, and by the biting taste which it imparts to the alcoholic extract; mineral substances by incineration. The amount of adulteration may be approximately judged of by determining the quantity of fixed oil obtainable from the mustard, which with pure mustard amounts to 35 or 36 per cent. (A. H. Allen, *Chem. News*, xxx. 116).

In the oil obtained by pressure from the seeds of black mustard, G. Goldschmiedt (*Wien. Akad. Ber.* lxx. 451) has found erucic and benic acids, together with a liquid acid not yet investigated (see ERUCIC ACID, p. 737).

MUSTARD OILS (VOLATILE). See CARBIMIDES (THIO-), (pp. 606-608).

MYCORAPHIN and **MYCOSTERIN**. These names are given by F. A. Hartzen (*Chem. Centr.* 1873, 205) to two substances which he obtained from *Agaricus fasciculatus* and *Lactarius deliciosus*.

MICROCYMES or **MICROZYMES**. See FERMENTS (p. 782).

MYELIN. On the formation of this substance from hæmin, see p. 922.

MYOSIN. See PROTEIDS.

MYRICYL ALCOHOL, $C^{20}H^{42}O = C^{20}H^{39}.CH^2OH$; also called *Melissyl Alcohol*. This alcohol and several of its derivatives have been studied by L. v. Pieverling (*Liebig's Annalen*, clxxxiii. 344). The alcohol was prepared from Carnauba wax by one of the two following processes: (1). The wax is saponified by boiling with alcoholic potash, the alcohol distilled off after filtration, and the soap boiled with a solution of lead acetate. The yellow masses which separate out are washed, dried, and boiled with absolute ether. The wax alcohol crystallises out from the filtered solution in white glittering crystals, and is purified by repeated recrystallisation. (2). The soapy mass

is boiled with dilute hydrochloric acid, and the waxy masses which separate are washed and dried. They are then dissolved in boiling alcohol, the fatty acids removed by ammonium and barium chloride, and the residue, after distilling off the alcohol, is boiled with water and then dried. The myricyl alcohol is then extracted with boiling absolute ether, and purified by repeated recrystallisation. Both these methods yield about 11 per cent.

Myricyl alcohol crystallises from ether in small glittering white needles, which are scarcely soluble in cold alcohol, ether, or benzene, little soluble in cold chloroform, but easily soluble in these media when hot. At 85° it melts to a colourless oil, solidifying at 84° to a white wax. On analysis it gave numbers closely according with those for the formula $C^{30}H^{61}OH$, and not in accord with Maskelyne's formula, $C^{31}H^{63}HO$ (vi. 391).

Myricyl Iodide, $C^{30}H^{61}I$, was prepared by heating the alcohol to 120° , adding phosphorus and iodine by small portions, and at the end of the reaction dissolving the product in alcohol and crystallising from ligroin. It forms small white glistening plates without odour or taste, scarcely soluble in cold alcohol, ether, or benzene, but easily soluble in the same liquids when hot. At 69.5° it melts to a clear, colourless oil.

Myricyl Chloride, $C^{30}H^{61}Cl$, is prepared by acting with phosphorus pentachloride on myricyl alcohol, and heating the product first in a water-bath, and then in a current of hydrochloric acid, and purified by repeated solution in hot ether. It forms a pale yellow, waxy mass, melting at 64.5° , and without odour or taste. It is soluble in alcohol, ether, benzene, and ligroin, but does not crystallise from any of these media.

Myricyl Hydrosulphide, $C^{30}H^{61}SH$, formed by the action of an alcoholic solution of myricyl chloride on potassium sulphide, is an amorphous yellow powder, without colour or taste, slightly soluble in boiling ether, ligroin, and alcohol, easily soluble in boiling benzene and chloroform, forming yellow solutions. It melts at 94.5° to a yellow oil, which solidifies at 93° to a yellow amorphous mass.

Myricylamines.—By passing a stream of dry ammonia into melted myricyl iodide for more than twenty-four hours, boiling the whole pulverulent mass with alcohol, and crystallising the residue from benzene, a yellow, crystalline, heavy body is obtained, melting at 78° , nearly insoluble in boiling alcohol and ether, but readily soluble in boiling benzene, toluene, and chloroform. This body appears to be a mixture of the three bases, mono-, di-, and tri-myricylamine, which cannot be separated from one another.

MYRISTIC ACID, $C^{14}H^{28}O^2 = C^{13}H^{27}.CO^2H$. This acid exists in nutmegs, and may be separated therefrom by distillation, whereby an oil is obtained, together with a crystalline substance, which, when washed with cold and repeatedly crystallised from hot alcohol, forms colourless shining laminae, having when fresh the peculiar odour of nutmegs, but losing it by keeping. These crystals are insoluble in alcohol, melt at 54.5° , and give by analysis numbers agreeing with the formula $C^{14}H^{28}O^2$. The alcoholic solution has a faint acid reaction (Flückiger, *N. Rep. Pharm.* xxiv. 213).

Myristic acid is likewise obtained, together with a fragrant oil, by distilling iris root with water (Flückiger, p. 1095).

N.

NAPHTHALENE, $C^{10}H^8$. *Formation*.—This hydrocarbon is formed: 1. On passing the vapour of isobutylbenzene over heated lead oxide at a temperature at which isobutylbenzene alone is not altered (Wreden and Znatovicz, *Ber.* ix. 1606). 2. On passing oil of turpentine through a red-hot tube (Schulz, *ibid.* ix. 548). 3. On distilling colophony and gum-benzoin with zinc-dust (Ciamician, *ibid.* xi. 269). 4. On passing wood-tar through a red-hot tube (Letnocy, Atherberg, *ibid.* xi. 1210, 1222). 5. On heating dimethylaniline with bromine at 110° – 120° (Brunner and Brandenburg, *ibid.* xi. 697).

Properties.—In connection with his experiments on the simultaneous distillation of water and of bodies not miscible with water, when the latter are heated by the passage of a current of steam, Naumann has determined the vapour-tension of naphthalene to be 2 mm. at 15° , 9 mm. at 78° , and 20.5 mm. at 100° . The amounts of naphthalene and water which distilled over when steam was passed into naphthalene were as follows:

Barometer (corr.)	Temperature in liquid	Temperature in vapour	Ratio of naphthalene to water in distillate
795.5	97.8°	99.2°	100 : 520
757	97.7°	99.1°	100 : 570
733		98.2°	100 : 555

(Ber. iv. 646; x. 2014, 2100; xi. 33).

The crystallographic characters of a number of allied chlorinated and brominated derivatives of naphthalene have been studied by Hintze (*Pogg. Ann. Sup.* vi. 1873, 177).

Reactions.—Naphthalene combines with α -dinitrochlorobenzene, forming the compound $C^{10}H^8, C^6H^3Cl(NO_2)_2$, which crystallises from alcohol in long white needles melting at 78°. It is decomposed when heated with an alkali or aniline, naphthalene being separated, and a dinitrophenol-salt or dinitrophenylaniline produced (Willgerodt Ber. xi. 603).

Thionyl chloride, $SOCl_2$, and naphthalene furnish only a resinous product (Böttiger, *ibid.* xi. 1409). Benzenesulphonic chloride, $C^6H^5.SO_2Cl$, and naphthalene, in presence of aluminium chloride, furnish a similar product (Beckurts a. Otto, *ibid.* xi. 2069).

HYDROCARBONS, &C., RELATED TO NAPHTHALENE.

Naphthalene Hydrides. By heating naphthalene at 280° with twenty times its weight of a solution of hydriodic acid, saturated at 0°, Berthelot obtained a hydrocarbon boiling at 200°–210°, which he regarded as *naphthalene dihydride*, $C^{10}H^{10}$, together with a small quantity of a second hydrocarbon, probably the tetrahydride, $C^{10}H^{12}$. This latter hydrocarbon was subsequently prepared in the pure state by Baeyer, by heating naphthalene with phosphonium iodide; according to Graëbe (*Ber.* v. 678), it is much more readily obtained by heating naphthalene with hydriodic acid and amorphous phosphorus (10 grams naphthalene, 3-grams phosphorus and 9 grams of a solution of hydriodic acid boiling at 127° are sealed up in a tube, which is heated for six to eight hours at 220°–250°).

Naphthalene tetrahydride has a density of .981 at 12.5°, and boils at 205°; it readily combines with trinitrophenol. It is dissolved by cold concentrated sulphuric acid, being converted into the sulphonic acid, $C^{10}H^{11}.SO_3H$. When passed through a red-hot tube, it is resolved into naphthalene and hydrogen. It is much more readily oxidised than naphthalene, yielding phthalic acid; the oxidation may be effected either by means of dilute nitric acid (sp. gr. 1.2), or by an acid solution of potassium permanganate. On treatment with concentrated nitric acid, it yields nitro-compounds, and among others trinitrophenol. On adding bromine to its solution in carbon disulphide, hydrobromic acid is evolved in large quantity, and on evaporating off the solvent, an oil is obtained, which decomposes on distillation into brominated compounds, naphthalene, and a hydrocarbon boiling at 210°–212°, which, perhaps, has the composition $C^{10}H^{10}$.

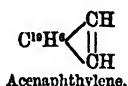
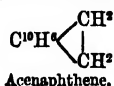
Wroden a. Znatowicz state (*ibid.* ix. 278, 1606; *Liebig's Annalen*, clxxxvii. 164) that the hydrocarbons $C^{10}H^{14}$, $C^{10}H^{16}$, $C^{10}H^{18}$, and $C^{10}H^{20}$ are also formed on heating naphthalene with hydriodic acid and phosphorus, but they have only described the manner in which they prepared one of these, viz. that of the formula $C^{10}H^{20}$, which they term *hexhydrocymene*. This hydrocarbon is said to be a colourless mobile liquid, having a density of .802 at 0° and .788 at 23°; it boils at 153°–158°, and is not attacked by either nitric or sulphuric acid at the ordinary temperature. No reason for terming this hydrocarbon *hexhydrocymene* has been stated. The hex- and oct-hydrides are said to boil respectively at 195°–200° and 185°–190°, and to absorb oxygen on exposure to the air.

Acenaphthylene, $C^{12}H^8$. This hydrocarbon is formed by passing acenaphthene, $C^{12}H^{10}$, over gently heated lead monoxide (Behr a. van Dorp, *Ber.* vi. 753; Blumenthal, *ibid.* vii. 1092). It is very soluble in alcohol, ether, and benzene, and is thus distinguished from acenaphthene, which is difficultly soluble. Acenaphthylene forms large, glistening, golden-yellow plates, melting at 92°–93°; it boils at about 265°–275°, but undergoes partial decomposition. With trinitrophenol it forms the compound $C^{12}H^8.C^6H^3(NO_2)_3OH$, which crystallises in yellow glistening needles, melting at 201°–202°. It is converted into acenaphthene on treatment of its alcoholic solution with sodium amalgam. On oxidation with potassic dichromate and sulphuric acid it yields naphthalic (naphthophthalic) acid, $C^{10}H^4(COOH)_2$. Acenaphthylene combines with bromine, forming a dibromide which yields naphthalic acid on oxidation. This bromide separates from a mixture of benzene and anhydrous alcohol in white needles melting at 121°–123°; by the action of alcoholic potash, it is converted into an oily monobromacenaphthylene, but a second molecule of hydrobromic acid cannot be withdrawn from this compound even by heating with alcoholic potash at 140°. On

treating bromacenaphthylene with bromine, dibromacenaphthylene is produced; this body crystallises in orange-red plates, and apparently yields bromonaphthalic acid on oxidation.

By treating a solution of acenaphthene in carbon disulphide with an excess of bromine, dibromacenaphthene tetrabromide, $C^{12}H^8Br^4$, is produced; but if a single molecular proportion of bromine be added to an ethereal solution of acenaphthene, monobromacenaphthene is formed. The latter yields monobromonaphthalic acid on oxidation.

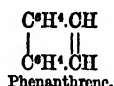
The relation between acenaphthene, acenaphthylene and naphthalic acid is represented by the following formulæ:



Methylnaphthalene, $C^{11}H^{10} = C^{10}H^7.CH^3$. This hydrocarbon appears to be formed on distilling colophonium and gum benzoin with zinc dust (Ciamiciu, *Ber.* xi. 269).

Phenylnaphthalene, $C^{16}H^{12} = C^8H^5.C^{10}H^7$. This hydrocarbon is formed on passing a mixture of naphthalene and bromobenzene through a tube heated to redness. It forms colourless transparent plates, melting at $95^\circ-96^\circ$ (Watson Smith, *Ber.* xii. 1396, 2049). The hydrocarbon produced on distilling chrysoquinone with soda-lime (viii. 472) is probably phenylnaphthalene.

By passing phenylnaphthalene vapour through a red-hot tube, Graebe and Bungener have succeeded in obtaining chrysene (*Ber.* xii. 1078), thus proving that chrysene is analogous in constitution to phenanthrene:



The phenylnaphthalene employed for this purpose was prepared by submitting naphthalene to the combined action of aluminium chloride and phenylacetic chloride, $C^8H^5.CH^2.COCl$, and reducing the naphthylbenzyl-ketone thus obtained by heating it with hydriodic acid and phosphorus at $150^\circ-160^\circ$.

Benzyl-naphthalene, $C^{17}H^{14} = C^{10}H^7.CH^2.C^7H^5$, prepared by digesting a mixture of naphthalene and benzyl chloride with zinc dust, crystallises in monoclinic prisms, melting at 58.6° . It boils at $320^\circ-330^\circ$. It is only slightly soluble in alcohol, but readily dissolves in ether and carbon disulphide. It yields non-crystalline derivatives with chlorine; monobromobenzyl-naphthalene is a syrup; the higher bromo-derivatives form granular masses. Nitric acid converts it into a trinitro-compound. It forms a crystalline compound with trinitrophenol (Miquel, *Bull. Soc. Chim.* [2], xxvi. 2).

Dinaphthyl, $C^{20}H^{14} = C^{10}H^7.C^{10}H^7$. On treating naphthalene potassium (vi. 844) with ethyl bromide, a yellow hydrocarbon is obtained which, according to Abeljanz (*Ber.* v. 1027), has the composition $C^{20}H^{12}$. Probably this may have been impure dinaphthyl. In addition to the two isomeric dinaphthyls already described (vii. 842), Watson Smith has obtained a third modification, thus completing the series of possible isomeric forms of this hydrocarbon. It would appear that all three are obtainable, though in very different quantities, by passing naphthalene, together with antimony trichloride, through a red-hot tube. By far the largest proportion of the product consists of isodinaphthyl; the next in quantity is the isomeride of lowest melting point; the third modification, identical with that originally obtained by Lossen, is formed by this method in extremely small quantity. The three bodies are separated by a tedious process of fractional crystallisation from low boiling petroleum (*Chem. Soc. J.* 1877, xxxii. 559; 1879, xxxv. 224).

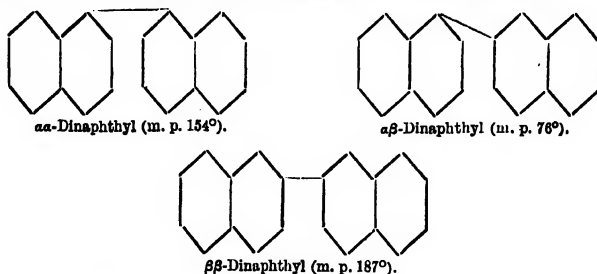
Watson Smith finds that the product prepared by Lossen's method, but using sulphuric acid diluted with rather more than its own bulk of water instead of with twice its weight of water, contains only the one dinaphthyl; this crystallises in perfectly colourless rhomboidal plates, melting at $154^\circ-155^\circ$. This modification is doubtless $\alpha\alpha$ -dinaphthyl, as Lossen also obtained it by the action of sodium-amalgam on α -bromonaphthalene.

So-called *isodinaphthyl* is probably the $\beta\beta$ -modification, as it has the highest melting point of any of the dinaphthyls. It crystallises readily in colourless, very regular rhombic plates, melting at 187° , and is much less soluble in alcohol, ether, benzene, &c. than either of the isomerides.

The third dinaphthyl, which is probably the $\alpha\beta$ -modification, forms small white

six-sided (apparently monoclinic) plates, melting at 76° . It is very soluble in alcohol, ether, and benzene.

All the dinaphthyls boil considerably above 300° , but the most fusible appears to have a lower boiling point than the least fusible. Their vapour-densities, as determined by Meyer's method, agree with the formula $C^{20}H^{14}$. On the supposition that they are constituted as above stated, they are indicated by the following symbols:



A number of experiments have been made by Watson Smith on the action, at a high temperature, of different chlorides on naphthalene. A mixture of naphthalene and antimony trichloride gives a much larger yield of high boiling products (dinaphthyls, &c.) than naphthalene alone; and similar results are obtained with tin tetrachloride. A mixture of naphthalene and tetrachloromethane nearly in the proportion $4C^{10}H^8 : CCl_4$, at a dull red heat, gave a better yield of dinaphthyls—as in other similar cases, chiefly the $\beta\beta$ -modification—than any other mixture at so low a temperature; similar but somewhat less satisfactory results were obtained with trichloromethane. Carbon disulphide does not appear to aid the formation of the dinaphthyls. A mixture of naphthalene and bromonaphthalene in equal molecular proportions yields a considerable quantity of $\beta\beta$ -dinaphthyl. Better results are obtained on passing this mixture over soda-lime; lime alone does not answer so well. Iso- ($\beta\beta$) dinaphthyl yields hexchlorobenzene and hexchloroethane on perchlorination (Watson Smith, *Ber.* xii. 2131).

Dinaphthylethane. A trichlorinated derivative of this hydrocarbon is formed in two isomeric modifications by the action of chloral and sulphuric acid on naphthalene (Grabowski, *Ber.* vi. 224; xi. 298). To a mixture of 3 pts. chloral, 8 pts. naphthalene and 6 pts. chloroform, 6 pts. of ordinary concentrated and afterwards an equal quantity of fuming sulphuric acid are added with constant stirring, the mixture being cooled. As soon as the temperature ceases to rise, 15–20 pts. of water are added, the chloroform is then distilled off, the residue washed with cold water, and afterwards extracted with 10–15 pts. of boiling water. The undissolved portion is then boiled with an equal weight of benzene, and the solution filtered; on cooling, it deposits crystals of β -dinaphthyltrichlorethane, $CCl_3.CH(C^{10}H^7)^2$. The α -compound is contained in the alcoholic solution, but has not yet been obtained free from the β -compound.

β -Dinaphthyltrichlorethane forms triclinic prisms melting at 156° ; it is insoluble in cold alcohol, and sparingly soluble in boiling alcohol and ether, but easily soluble in benzene and chloroform. It is not oxidised by the ordinary chromic acid mixture. It yields a bromo-derivative on treatment with bromine. When submitted to the action of 10 pts. of cold fuming nitric acid, it is converted into a tetranitro-derivative, which is a pale yellow crystalline powder melting at 258° .

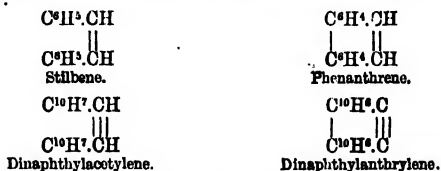
β -Dinaphthyltrichlorethane, $CCl_3.CH(C^{10}H^7)^2$, is obtained on submitting β -dinaphthyltrichlorethane to dry distillation or to the action of alcoholic potash. It crystallises from benzene, in which it is very easily soluble, in short prisms melting at 219° , difficultly soluble in alcohol; it boils without decomposition above 360° . It combines with bromine. With nitric acid it yields tetranitro- β -dinaphthyltrichlorethane, which melts at 292° .

α -Dinaphthyltrichlorethane is produced on distilling crude α -dinaphthyltrichlorethane with 20 per cent. of its weight of lime. The product is dissolved in the smallest possible quantity of hot benzene, and after the β -compound has crystallised out, the benzene is distilled off, and the residue crystallised from boiling alcohol, from which it separates in long, colourless, silky needles, melting at 150° .

Dinaphthylacetylene, $C^{22}H^{14} = C^{10}H^7.C \equiv C.C^{10}H^7$. This hydrocarbon is formed on heating dinaphthyltrichlorethane with zinc dust, lead oxide, zinc oxide, or

soda-lime. It crystallises from alcohol in long silky needles, melting at 225° , and boils above 360° , but apparently undergoes decomposition.

Dinaphthylanthrylene, $C^{22}H^{12}$. This hydrocarbon is formed under apparently the same conditions as the foregoing. It is best prepared by distilling β -dinaphthyl-trichlorethane with 15 pts. zinc oxide at a red heat. It is difficult to purify. After crystallisation from benzene and sublimation, it forms violet-coloured plates, melting at 270° ; but when separated from its compound with trinitrophenol, it is colourless. Probably it bears the same relation to dinaphthylacetylene that phenanthrene bears to stilbene, thus:



Naphthylphenylcarbinol and Dinaphthylphenylmethane. See LKHN (Ber. xiii. 358).

Naphthylphenylcarbazol, $C^{16}H^{11}N$. Graebe a. Knecht have described a compound of the formula $C^{16}H^{11}N$, obtained from coal-tar, and by passing the vapour of β -phenylnaphthylamine through a red-hot tube, which appears to be the analogue of imidodiphenyl (carbazol), $C^{12}H^9N$ (Ber. xii. 341, 2242), thus:



This compound was first discovered by Brunck in a sublimate from the residue of the distillation of crude anthracene, and purified by him, in conjunction with Vischer, by crystallising the portion of the sublimate insoluble in boiling glacial acetic acid from hot aniline and then subliming it. Graebe a. Knecht, however, employ benzene instead of aniline. When purified by crystallisation or sublimation, it always possesses an intense greenish-yellow or golden-yellow colour, which, however, does not appear to be characteristic of the pure substance, as it is rendered colourless, if heated with potassium hydrate, without being otherwise altered in properties, and is also obtained colourless when separated from its acetyl-derivative.

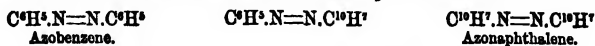
It is almost insoluble in cold alcohol and benzene, very slightly soluble in boiling benzene and acetic acid, moderately soluble in hot aniline. Its solutions exhibit an intense blue fluorescence. It melts at 330° , and has a higher boiling point than sulphur; its vapour-density, determined in phosphorus pentasulphide vapour, agrees with the formula $C^{16}H^{11}N$. It dissolves in sulphuric acid, forming a yellow solution; the least trace of nitrous or nitric acid renders the liquid brownish-green.

Heated with acetic anhydride at 220° – 240° , it yields a *monacetyl-derivative*, $C^{16}H^{10}N(C^2H^3O)$, which crystallises from boiling alcohol in colourless prisms melting at 121° . By the action of nitrous acid, it is converted into a *nitroso-derivative*, $C^{16}H^{10}N(NO)$, which crystallises from ether in reddish-yellow needles melting at 240° . This nitroso-derivative dissolves in sulphuric acid, producing a magnificently red-violet coloured liquid, which becomes dark brown on heating.

It is with difficulty oxidised by chromic acid, yielding one or more acids and a quinone, $C^{16}H^8N(O^2)$.

Naphthalene Colours. *Naphthalene* or *Magdala-red* (Hofmann, Ber. ii. 374, 412).—This colour has the formula $C^{20}H^{11}N^3$, and is a product of the action of naphthylamine on the so-called azodinaphthylidiamine of Perkin and Church, $C^{20}H^{15}N^3 + C^{10}H^9N = C^{30}H^{24}N^3 + NH^3$. An analogous compound having similar properties is obtained on submitting azodinaphthylidiamine to the action of paratoluidine hydrochloride (Lecco, Ber. vii. 1290). Azodinaphthylidiamine, according to Lecco, melts at 174° , and not at 135° , as stated by Perkin a. Church.

A considerable number of azo-derivatives, prepared by the direct action of diazo-compounds on various naphthalene-derivatives, are now in use as dyes. The following compounds of this class have been described by Griess, Hofmann, Typke and Witt. It will be noticed that they are all derivatives of the azo-compound intermediate in composition between so-called azobenzene and azonaphthalene, thus:



See also Weselsky and Benedikt and Griess (Ber. xii. 238, 426).

(a). $C^6H^3.N=N.C^10H^4(OH)$.—The compound of this formula is the product of the action of diazobenzene nitrate on α -naphthol. It forms microscopic brown needles, melting at 166° , soluble in alkalis and most of the ordinary solvents; its solutions have a reddish-brown colour and possess considerable tinctorial power. On treatment with sulphuric acid, it is converted into a sulpho-acid, which dyes silk and wool orange-yellow (Typke, *Ber.* x. 1580).

(b). $C^6H^3.N=N.C^10H^4(SO^3H).OH$.—The compound of this formula is prepared by adding a solution of sodium α -naphtholsulphonate to a solution of diazobenzene nitrate; it crystallises in hair-fine red needles (Hofmann, *Ber.* x. 1380).

(c). $C^6H^3.N=N.C^10H^3(SO^3H).OH$.—This compound is prepared in a similar manner from β -naphtholsulphonate; it forms reddish-brown needles with a golden-green lustre (Griess, *ibid.* 2197).

(d, e). $C^6H^4(SO^3H).N=N.C^10H^4(OH)$.—Two modifications of this compound, prepared by the action of paradiazobenzenesulphonate (from paramidobenzenesulphonic or sulphanilic acid) on α - and β -naphthol respectively, are the basis of Poirrier's oranges and of the so-called Tropæolines 000 1 and 2 (comp. Witt, *Chem. Soc. J.* xxxv. 184).

(f, g). Two other modifications of the same compound may be obtained by the action of metadiazobenzenesulphonate on α - and β -naphthol (Griess, *loc. cit.*)

When submitted to the action of nascent hydrogen (tin and hydrochloric acid) these compounds yield the corresponding amidosulphonic acid and amidonaphthol (Griess).

(h). $C^6H^4(SO^3H).N=N.C^10H^4(SO^3H).OH$.—This compound is prepared by adding a solution of paradiazobenzenesulphonate to an alkaline solution of β -naphtholsulphonic acid, &c. It is a yellowish-red crystalline substance. The barium salt, $C^6H^4N^2S^2O^6Ba.7.5OH^2$, crystallises in dark orange-red microscopic needles, difficultly soluble in hot and very difficultly soluble in cold water.

(i). $C^6H^4(SO^3H).N=N.C^10H^4.OH$.—This body is a beautiful red colour; it is prepared from diazonaphthalenesulphonic acid and β -naphthol (Griess; comp. *Ber.* xiii. 268).

(j). $C^6H^4(SO^3H)(COOH).N=N.C^10H^3(OH)(COOH)$.—This compound is obtained by acting on an alkaline solution of α -hydroxynaphthoic acid with diazosulphobenzoic acid; it crystallises in brown microscopic needles and plates, exhibiting a bronze lustre (Griess).

(k). $C^6H^2Br^2(SO^3H).N=N.C^10H^2(OH)^2$.—This compound is prepared from dihydroxynaphthalene and diazodibromobenzenesulphonic acid; it separates from its aqueous solution on the addition of hydrochloric acid in violet-brown microscopic needles (Griess).

DERIVATIVES OF NAPHTHALENE.

Chloronaphthalenes. *Monochloronaphthalenes*, $C^{10}H^7Cl$.—That obtained by the direct action of chlorine on naphthalene—or rather, by the decomposition of naphthalene dichloride—is the α -modification. β -*Monochloronaphthalene* is formed on treatment of β -naphthol or naphthalene- β -sulphonic chloride with phosphoric pentachloride (Rimarenko, *Ber.* ix. 663; Cleve, *Bull. Soc. Chim.* xxv. 257); and by boiling β -diazonaphthalene sulphate with concentrated hydrochloric acid (Liebermann a. Palm, *Liebig's Annalen*, clxxxiii. 275). It crystallises from alcohol, in which it is easily soluble, in naphthalene-like plates melting at 61° (L. a. P.); 56° (R.). It boils at about 260° .

Dichloronaphthalenes, $C^{10}H^6Cl^2$.—No fewer than eight of the ten possible modifications of dichloronaphthalene are said to have been obtained.

α -*Dichloronaphthalene*, obtained by acting on naphthalene tetrachloride with alcoholic potash, melts at 35° , and boils at 281° (Faust a. Saame).

β -*Dichloronaphthalene* is formed, together with a small amount of the α -isomeride, when pure naphthalene tetrachloride is decomposed by rapidly heating small quantities to the boiling point, but together with a considerable amount of the same isomeride, when a larger quantity of the tetrachloride is heated and maintained in a state of gentle ebullition until hydrochloric acid is no longer evolved (Krafft a. Becker, *Ber.* ix. 1088). It is also formed on treatment of α -nitro- α -naphthol with phosphoric pentachloride (Atterberg, *ibid.* ix. 1189). It melts at 68° and boils at 281° (Faust a. Saame); on oxidation with nitric acid, it yields dichlorophthalic acid (Atterberg, *ibid.* x. 647).

γ -*Dichloronaphthalene* is best prepared by gradually adding phosphoric pentachloride to so-called α -dinitronaphthalene heated in an oil bath to its melting point, the apparatus being so arranged that the phosphoric oxychloride distils over as it is

produced; it is a product of the action of chlorine on nitronaphthalene (Atterberg, *ibid.* ix. 317, 1188, 1734), and of the action of phosphoric pentachloride on the nitronaphthalenesulphonic acid formed from α -nitronaphthalene and from naphthalene- α -sulphonic acid (Cleve, *Bull. Soc. Chim.* xxiv. 506). γ -Dichloronaphthalene crystallises from alcohol in colourless glistening scales melting at 107°. On oxidation with nitric acid, it yields nitrochlorophthalic acid, $C^8H^5Cl(NO_2)(COOH)$.

δ -Dichloronaphthalene is obtained on distilling the chloride of α - and ϵ -dichloronaphthalene that of β -naphthalenedisulphonic acid with phosphoric pentachloride. The former crystallises in large brilliant plates melting at 114°; the latter in brilliant prisms melting at 135° (Cleve *Bull. Soc. Chim.* xxvi. 244).

ζ -Dichloronaphthalene is formed in small quantity on distilling β -dinitronaphthalene with phosphoric pentachloride; it crystallises in well-developed prisms, melting at 83° (Atterberg, *Ber.* ix. 1732).

η -Dichloronaphthalene, obtained by distilling nitronaphthalene- β -sulphonic chloride (m.p. 125.5°), with phosphoric pentachloride, melts at 48°. It yields a mixture of chloro- and chloronitrophthalic acid when submitted to the action of nitric acid under pressure at 150° (Cleve, *Bull. Soc. Chim.* xxix. 499).

θ -Dichloronaphthalene is obtained in like manner from the isomeric chloride melting at 169°. It forms small white needles melting at 61.5° (Cleve, *ibid.* xxix. 414, 450).

Trichloronaphthalenes, $C^{10}H^3Cl^3$.—Six of these are now known:

α -Trichloronaphthalene, obtained by boiling α -chloronaphthalene tetrachloride with alcoholic potash, melts at 131.5°; it yields nitrotrichlorophthalic acid when heated with nitric acid at 200° (Widmann, *Bull. Soc. Chim.* xxviii. 511).

β -Trichloronaphthalene is one of the products of the action of chlorine on nitronaphthalene; it forms long pliable needles melting at 90° (Atterberg, *Ber.* ix. 926).

γ -Trichloronaphthalene is also formed by the action of chlorine on nitronaphthalene (Atterberg, *ibid.* ix. 316), and by distilling dichloronaphthalene- α -sulphonic chloride with phosphoric pentachloride (Widmann, *ibid.* xii. 2230). It crystallises in brittle glistening needles melting at 103°.

δ -Trichloronaphthalene may be obtained by distillation of β -dinitronaphthalene, nitro- γ -dichloronaphthalene, α -dinitrochloronaphthalene, β -dinitrochloronaphthalene, and nitro- β -dichloronaphthalene with phosphoric pentachloride (Atterberg, *ibid.* ix. 1187, 1733). It forms very long, flat, pliable needles, melting at 131°; heated with nitric acid, it yields a dichlorophthalic acid.

ϵ -Trichloronaphthalene, prepared by acting upon nitro- η -dichloronaphthalene with phosphoric pentachloride, crystallises in colourless needles melting at 65° (Cleve, *Bull. Soc. Chim.* xxix. 499).

ζ -Trichloronaphthalene, prepared by distilling dichloronaphthalene- β -sulphonic chloride with phosphoric pentachloride, crystallises in fine white pliable needles melting at 76°; it apparently yields nitrodichlorophthalic acid when heated with nitric acid (Widmann, *Ber.* xii. 962).

Tetrachloronaphthalenes, $C^{10}H^2Cl^4$.—Five modifications have been described:

α -Tetrachloronaphthalene, obtained by acting with alcoholic potash on the dichlorotetrachloride formed on chlorinating naphthalene, melts at 130° (Faust a. Seame).

β -Tetrachloronaphthalene is formed on chlorinating nitronaphthalene; it crystallises in needles, very difficultly soluble in alcohol, melting at 194° (Atterberg, *ibid.* ix. 318).

γ -Tetrachloronaphthalene, formed from the isomeric dichlorotetrachloride from naphthalene, melts at 176° (Widmann, *ibid.* x. 1725).

δ -Tetrachloronaphthalene, from γ -dichloronaphthalene tetrachloride, crystallises in fine white needles melting at 141° (Atterberg a. Widmann, *Ber.* x. 1842).

ϵ -Tetrachloronaphthalene, obtained by distilling dinitro- γ -dichloronaphthalene with phosphoric pentachloride, melts at 180° (Atterberg a. Widmann, *loc. cit.*)

Pentachloronaphthalenes, $C^{10}H^1Cl^5$.—In addition to that described by Graebe, a second modification is known, obtained by distilling nitro- δ -tetrachloronaphthalene with phosphoric pentachloride; it melts at 177°, and on oxidation with nitric acid yields trichlorophthalic acid (Atterberg a. Widmann, *loc. cit.*)

Octochloronaphthalene, $C^{10}Cl^8$, according to Ruoff (*ibid.* ix. 1486), melts at 203° and not at 135° as stated by Berthelot and Jungfleisch (vi. 847). When heated with antimony pentachloride at 280°–300°, it is resolved into hexachlorobenzene, hexachlorethane, and tetrachloromethane.

Naphthalene and Chloronaphthalene Chlorides, *Naphthalene dichloride*, $C^{10}H^8Cl^2$, is obtained, according to E. Fischer (*Ber.* xi. 735, 1411), together with two isomeric tetrachlorides and a monochloronaphthalene dichloride on chlorinating naphthalene according to Depouilly's process, by treatment with potassic chlorate and hydrochloric acid. It has the properties ascribed to it by Lauront. It begins slowly

to decompose at 40° – 50° ; when heated with sodium or sodium amalgam in sealed tubes at 150° , it is reconverted into naphthalene.

α-Naphthalene tetrachloride, $C^{10}H^4Cl^4$. According to Grimaux (*Ber.* 1872, v. 222; also Schwarzer, *Ber.* x. 379) a saturated solution of chlorine in chloroform at once converts naphthalene into this compound, a pure product being readily obtained. It melts at 182° (vi. 846); and yields almost the theoretical amount of phthalic acid on oxidation with nitric acid (E. Fischer). When decomposed by alcoholic potash, it appears to yield only *α*-dichloronaphthalene. If, however, it be heated in small quantities (about 1 gram) at a time, as rapidly as possible, to the boiling point, and vigorously boiled for a few minutes, it is almost entirely converted into *β*-dichloronaphthalene; but if a larger quantity be heated and maintained in gentle ebullition as long as hydrochloric acid is evolved, a considerable amount of *α*-dichloronaphthalene is also produced (Krafft a. Becker, *Ber.* ix. 1088). If an alcoholic or ethereal solution of naphthalene tetrachloride be digested with zinc, naphthalene is reproduced (Zinin, *ibid.* iv. 288).

β-Naphthalene tetrachloride, according to E. Fischer, melts at 116° – 118° ; Atterberg doubts the formation of this modification (*ibid.* xi. 1223).

Monochloronaphthalene dichloride, $C^{10}H^7Cl^2$, melts at 176° (E. Fischer).

Monochloronaphthalene tetrachloride, $C^{10}H^7Cl^3$.—That obtained from *α*-chloronaphthalene melts at 131.5° . The isomeride from *β*-chloronaphthalene is an oil (Widmann, *ibid.* x. 1724; *Bull. Soc. Chim.* xxviii. 505).

Dichloronaphthalene tetrachloride, $C^{10}H^6Cl^4$.—*α*-Dichloronaphthalene yields two tetrachlorides, one of which melts at 172° ; the other is an oil. *β*-Dichloronaphthalene tetrachloride, from *β*-dichloronaphthalene, melts at the same temperature (172°) as, and in other respects closely resembles, crystalline *α*-dichloronaphthalene tetrachloride. On submitting *γ*-dichloronaphthalene dissolved in chloroform to the action of chlorine, a tetrachloride is obtained which crystallises in prisms melting at 85° (Atterberg a. Widmann, *ibid.* x. 1842).

Trichloronaphthalene dichloride, $C^{10}H^5Cl^3$, is known in two modifications: one obtained by acting on *γ*-dichloronaphthalene dissolved in chloroform with chlorine; the other by similarly treating a solution of *α*-chloronaphthalene in acetic acid. The former crystallises in large glistening prisms melting at 93° (Atterberg a. Widmann); the latter melts at 152° (Widmann).

Bromonaphthalenes. ***β-Bromonaphthalene***, obtained by decomposing *β*-diazonaphthalene perbromide by boiling it with alcohol, crystallises in colourless plates melting at 68° ; it is easily soluble in alcohol, ether, benzene, and chloroform (Liebermann a. Palm, *Lichig's Annalen*, clxxxiii. 269).

Dibromonaphthalenes, $C^{10}H^6Br^2$.—The dibromonaphthalene melting at 81° , which is the chief product of the direct action of bromine on naphthalene (vi. 845), probably corresponds in constitution to *β*-dichloronaphthalene (comp. p. 1378). The isomeric modification which is formed simultaneously, according to Jolin (*Bull. Soc. Chim.* xxviii. 514), melts at 61° and not at 76° as stated by Glaser. By displacing the NH^2 -group in dibromonaphthylamine (m. p. 118°) by hydrogen, Meldola has prepared a dibromonaphthalene which crystallises in white needles melting at 64° (*Ber.* xii. 1961). It is noteworthy that this modification differs totally in appearance from Jolin's dibromonaphthalene, melting at 61° , which is probably analogous in constitution to *α*-dichloronaphthalene. *β*-Dibromonaphthalene may also be obtained by distilling *α*-bromonaphthalenesulphonic bromide or nitro-*α*-bromonaphthalene with phosphoric pentabromide (Jolin). By distilling nitro-*β*-dibromonaphthalene with PBr^3 , a tribromonaphthalene (*β*) is produced, which crystallises in long flexible needles melting at 85° (Jolin).

γ-Dibromonaphthalene is formed by the action of phosphoric pentabromide on *α*-dinaphthalene. It crystallises in brilliant scales melting at 129° (Jolin).

δ-Dibromonaphthalene is formed by distilling naphthalene-*α*-disulphonic acid with phosphoric pentabromide; it crystallises in thin plates, melting at 140.5° (Jolin).

The dibromonaphthalene melting at 126° obtained by Darmstädter and Wichelhaus (vi. 845) was probably the *γ*-modification.

Tribromonaphthalenes.—In addition to the *α*-modification (m. p. 75° Glaser) and that described above, a third modification (*γ*) is known, produced by treating naphthalene-*β*-sulphonic acid with bromine, and distilling the dibromosulphonic acid with PBr^3 . It crystallises in short brittle needles melting at 86.5° (Jolin).

Hexbromonaphthalene, $C^{10}H^2Br^6$, is obtained by submitting naphthalene to the prolonged action of bromine in presence of iodine, finally at 350° . It closely resembles hexbromobenzene in appearance; it is soluble, although not readily, in hot chloroform,

benzene, toluene, and aniline, but insoluble in alcohol and ether. It sublimes in felt-like masses of needless melting at 245° (Gessner, *Ber.* ix. 1510).

Nitrochloronaphthalenes. *α -Mononitrochloronaphthalene*, $C^{10}H^9(NO^2)Cl$, prepared by acting upon α -chloronaphthalene with cold nitric acid (sp. gr. 1.4), crystallises from alcohol in concentrically grouped, extremely fine, pale-yellow needles, melting at 85° ; on prolonged digestion with tin and hydrochloric acid, it yields α -naphthylamine (Atterberg, *Ber.* ix. 927).

α -Dinitro- α -chloronaphthalene, $C^{10}H^8Cl(NO^2)_2$, is obtained, together with the foregoing, on nitration of α -chloronaphthalene with warm nitric acid of sp. gr. 1.4, and together with an isomeric modification when the fuming acid is employed. It crystallises in long yellow pliable needles, easily soluble in hot alcohol; it melts at 106° (Faust a. Seame; Atterberg).

β -Dinitro- α -chloronaphthalene.—This appears to be formed in relatively larger quantity the higher the temperature of nitration. It is difficultly soluble, even in boiling alcohol; it crystallises from glacial acetic acid in short, pale yellow, brittle needles, melting at 180° (Atterberg, *loc. cit.*).

Nitro- γ -dichloronaphthalene, $C^{10}H^7(NO^2)Cl_2$, prepared by nitrating γ -dichloronaphthalene with cold nitric acid (sp. gr. 1.4), forms short sulphur-yellow prisms, difficultly soluble in alcohol, melting at 142° (Atterberg, *loc. cit.*).

Dinitro- γ -dichloronaphthalene, $C^{10}H^6(NO^2)_2Cl_2$, formed by treating the mononitro-derivative with a mixture of nitric and sulphuric acids, crystallises in pale-yellow brittle prismatic needles, very difficultly soluble even in glacial acetic acid. It melts at 246° (Atterberg, *loc. cit.*).

Nitro- δ -tetrachloronaphthalene, $C^{10}H^4Cl_4(NO^2)$, prepared by the action of concentrated nitric acid on δ -tetrachloronaphthalene, crystallises from a mixture of toluene and alcohol in large pale-yellow rhombic plates melting at 154° (Atterberg a. Widmann, *ibid.* x. 1831).

Nitrobromonaphthalenes. *Nitro- α -bromonaphthalene*, $C^{10}H^9Br.NO^2$, formed by nitration of α -bromonaphthalene, crystallises from alcohol in yellow needles melting at 85° (Jolin, *Bull. Soc. Chim.* xxviii. 514).

An isomeric *bromonitronaphthalene* is obtained by displacing the NH^2 -group in bromonitro- α -naphthylamine by hydrogen. It crystallises in pale yellow needles, melting at 131° (Liebermann a. Hammerschlag, *Liebig's Annalen*, clxxxiii. 262).

Nitro- β -dibromonaphthalene, $C^{10}H^8Br_2.NO^2$, produced by the action of cold nitric acid of sp. gr. 1.4 on β -dibromonaphthalene, forms yellow needles melting at 116.5° (Jolin).

Nitronaphthalenes. *Nitronaphthalene*.—According to Guareschi (*ibid.* x. 294), α -nitronaphthalene (m. p. 58° – 59°) is the only mononitro-derivative obtained on nitrating naphthalene under very various conditions.

According to de Koninck and Marquardt (*ibid.* v. 11), nitronaphthalene boils at 304° . It is violently acted upon by phosphoric pentasulphide and pentachloride. If it be mixed with a slight excess of the latter in a retort, and the mixture be very gradually heated, phosphoric oxychloride passes over, the temperature rising gradually to about 120° , or to 150° if an excess of PCl_5 be employed; the residue then consists of monochloronaphthalene and a small amount of unaltered nitronaphthalene.

In a similar manner, nitronaphthalene yields a mixture of mono- and dibromonaphthalene (probably γ -di) when heated with an equal volume of a concentrated solution of hydrobromic acid at 195° (Baumbauer, *ibid.* iv. 926).

On oxidation with chromic acid, nitronaphthalene is converted into nitro-naphthalic acid (m. p. 212° ; Beilstein a. Kurbatow, *Ber.* xii. 608).

Dinitronaphthalenes.—In addition to the two modifications (α and β) formed simultaneously on nitration of naphthalene (vii. 834), which melt respectively at 216° and 170° , a third isomeride is known, obtained by displacing the NH^2 -group in dinitro- α -naphthylamine by hydrogen. It crystallises in almost colourless needles, melting at 144° (Liebermann a. Hammerschlag, *Liebig's Annalen*, clxxxiii. 272).

α -Dinitronaphthalene yields nitrophthalic and ordinary dinitrobenzoic acid, β -dinitronaphthalene dinitrophthalic and dinitrobenzoic acid, when oxidised with dilute nitric acid (Beilstein a. Kurbatow, *Ber.* xiii. 353).

Trinitronaphthalenes.—Three modifications of this derivative are known. If α -dinitronaphthalene be submitted to the prolonged action of fuming nitric acid, it yields *α -trinitronaphthalene*, melting at 122° , together with nitrophthalic acid (Aguiar, *Ber.* iv. 897). If, however, it is boiled for a few minutes with 10 pts. of a mixture of equal weights of fuming nitric and concentrated sulphuric acids, an isomeric *γ -dinitronaphthalene* is obtained (Beilstein a. Kuhlberg, *ibid.* vi. 647), and the same

modification is produced in almost theoretical amount if 150 grams of fuming nitric acid are poured on 9 grams of the dinitronaphthalene and 150 grams of sulphuric acid are then added, the mixture being poured into water as soon as it becomes cool (Aguilar). γ -Trinitronaphthalene crystallises from fuming nitric acid in glistening four-sided plates, and from alcohol in chloride of ammonium-like forms; it melts at 147° (B. a. K.); 164° (A). β -Dinitronaphthalene yields only β -trinitronaphthalene, whatever the conditions of nitration.

If α -dinitronaphthalene be boiled for several hours with double the quantity of the acid mixture used in converting it into trinitronaphthalene, fuming sulphuric acid also being employed in place of the ordinary acid, it is converted into α -tetranitronaphthalene (Beilstein a. Kuhlberg).

Nitrosonaphthalene, $C^{10}H^7(NO)$. To prepare this compound, a solution of mercury dinaphthyl in carbon bisulphide is mixed with a like solution of nitrosyl bromide—prepared by saturating a solution of bromine in carbon bisulphide at -20° with nitric oxide—in the proportions indicated by the equation: $(C^{10}H^7)^2Hg + NOBr = HgBr.C^{10}H^7 + C^{10}H^7(NO)$.

After purification, it forms yellow aggregates, which very rapidly become red on exposure to air; it melts at 84° , and decomposes at about 134° . Nitrosonaphthalene at once combines with aniline, forming a red substance; it dissolves in sulphuric acid, producing a cherry-red liquid; and if it be dissolved in phenol and sulphuric acid be added, a blue colour is produced (A. Baeyer, *Ber.* vii. 1639).

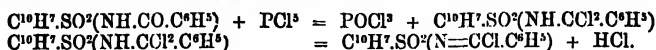
Azonaphthalene, $C^{10}H^7N^2 = C^{10}H^7.N \equiv N.C^{10}H^7$. This compound is formed in small quantity on heating nitronaphthalene with zinc-dust (Doer, *Ber.* iii. 291), and on oxidation of naphthylamine with lead oxide (Schichuzky, *ibid.* vii. 1454). The methods by which azobenzene is obtained from nitrobenzene are not applicable to its preparation (Klobukowski, *ibid.* x. 570; comp. 772 and 873). It is identical with Laurent's *naphthase* (Alexejeff, *ibid.* iii. 868; Klobukowski).

Azonaphthalene is very slightly soluble in alcohol, ether, benzene, chloroform, and acetic acid; it crystallises from a hot solution in acetic acid mixed with a couple of drops of fuming nitric acid in yellow needles, melting at 275° . It dissolves in concentrated sulphuric acid, forming a dark violet-blue liquid. It appears to combine with bromine, forming an unstable bromide. If heated with bromine at 260° , or only gently warmed with bromine in presence of iodine, it is converted into a pentabromo-derivative.

Naphthalenesulphonic Acids. At present, two monosulphonic acids, two disulphonic acids, and a tetrasulphonic acid are known. The two first mentioned have already been described (vi. 860; vii. 835), but the following derivatives require notice here:

Naphthalene- α -sulphonic chloride, $C^{10}H^7.SO^2Cl$, crystallises from ether in glistening plates melting at 66° , easily soluble in ether, carbon bisulphide, and benzene (Maikopar, *Zeits. Chem.* 1869, 710). By the action of chlorine on its solution in carbon bisulphide, the *tetrachloride*, $C^{10}H^7.Cl^4.SO^2Cl$, is produced. This compound does not appear to crystallise (Widmann, *Ber.* xii. 2228).

Naphthalene- α -sulphonamide, $C^{10}H^7.SO^2(NH^2)$, prepared by warming the chloride with a concentrated aqueous solution of ammonia, and purified by crystallisation from alcohol, melts at 150° ; it is soluble in water, and easily soluble in alcohol (Maikopar). When heated with the equivalent amount of benzoic chloride at 145° – 150° as long as hydrochloric acid is evolved, it is converted into the benzoyl derivative, $C^{10}H^7.SO^2(NH.CO.C^6H^5)$. To purify the product, it is washed with alcohol, dissolved in potassic carbonate solution, precipitated by acid, and crystallised from boiling alcohol. It then crystallises from alcohol, in which it is somewhat difficultly soluble, in four-sided prisms, melting at 194° – 195° . It possesses marked acid properties, decomposing carbonates, and forming metallic derivatives such as $C^{10}H^7.SO^2(NK.CO.C^6H^5)$, &c., and belongs to the class of so-called *aci-amides* (vii. 21; Welkow, *Zeits. Chem.* 1871, 422). If submitted to the action of phosphorus pentachloride, it is converted into the chlorinated compound $C^{10}H^7.SO^2(NC^7H^5Cl)$, this body being doubtless formed in accordance with the following equations:



The new compound crystallises from ether in large four-sided plates, melting at 93° . It is reconverted into the aciamide by boiling water or alcohol; and on treatment with ammoniac carbonate forms the amido-derivative $C^{10}H^7.SO^2(N \equiv C.NH^2.C^6H^5)$ (Wekow, *Ber.* v. 142).

Naphthalene- β -sulphonic chloride, $C^{10}H^7.SO^2Cl$, crystallises in plates; it is less soluble in ether than the α -chloride, and melts at 76° (Maikopar). Like the α -sulphonic

chloride, it is converted into a tetrachloride, $C^{10}H^7Cl^4.SO^2Cl$, by the action of chlorine. This latter crystallises from chloroform in hard colourless transparent cubes, melting at 131° , easily soluble in chloroform, carbon bisulphide, and boiling acetic acid (Widmann, *Ber.* xii. 960).

Naphthalene- β -sulphonamide, $C^{10}H^7.SO^2(NH^2)$, crystallises from boiling alcohol in small thin plates, difficultly soluble in water and ether (Maikopar); it melts at 217° (corr. Cleve).

Ethyl, phenyl, and naphthyl derivatives of naphthalene α - and β -sulphonamide have been described by Carlson (comp. *Ber.* x. 1725).

Chloronaphthalenesulphonic bromide, $C^{10}H^4Cl.SO^2Br$.—This compound is produced on treatment of sodium bromonaphthalenesulphonate with PCl^5 . It crystallises from ether in white needles melting at 115° (Gessner, *ibid.* ix. 1504).

Dichloronaphthalene- α -sulphonic chloride, $C^{10}H^5Cl^2.SO^2Cl$, is formed on decomposing the tetrachloride obtained from naphthalene- α -sulphonic chloride with alcoholic potash, and treating the resulting potassic salt, when sufficiently purified, with phosphoric pentachloride. It is easily soluble in benzene and boiling acetic acid, crystallising from the former in very large colourless well-formed glistening prisms, and from the latter in glistening scales or needles; it melts at 145° . When distilled with PCl^5 , it is converted into γ -trichloronaphthalene (Widmann).

Dichloronaphthalene- α -sulphonic acid, $C^{10}H^5Cl^2.SO^2(OH)$, prepared by heating the foregoing chloride with water at 140° , crystallises in long colourless glistening flat needles, somewhat soluble in cold water. Its salts are difficultly soluble, and crystallise either in needles or plates; several of them require heating nearly to 200° before they are completely deprived of their water of crystallisation. The *potassium* salt, $C^{10}H^5Cl^2.SO^2K.2H^2O$, crystallises in groups of fine white pliable needles; it loses 1 mol. of water under the desiccator, and the remaining molecule when heated at 185° ; 1 pt. of the salt dried at 100° dissolves in 115 pts. of water at 15° . The *sodium* salt, $C^{10}H^5Cl^2.SO^2Na.3OH^2$, forms long glistening flat prisms; it loses 1 mol. of water under the desiccator. The *calcium* salt, $(C^{10}H^5Cl^2.SO^2)^2Ca.4H^2O$, is very difficultly soluble in water, and crystallises from a hot concentrated solution in white glistening quadratic or rectangular plates. The *zinc* salt, $(C^{10}H^5Cl^2.SO^2)^2Zn.7H^2O$, forms glistening plates difficultly soluble in cold, but more easily in hot water. The *amide*, $C^{10}H^4Cl^2.SO^2(NH^2)$, crystallises from alcohol in flat feathery groups, melting above 250° (Widmann).

Dichloronaphthalene- β -sulphonic chloride, $C^{10}H^5Cl^2.SO^2Cl$, prepared in a similar manner to the above from the β -sulphonic tetrachloride, crystallises from benzene in thin white needles, grouped in ball-like forms; it melts at 133° . When distilled with PCl^5 , it yields ζ -trichloronaphthalene (Widmann).

Dichloronaphthalene- β -sulphonic acid, $C^{10}H^5Cl^2.SO^2(OH)$, obtained by decomposing the above chloride with water at 130° , is very soluble in hot, but only moderately in cold water. When a moderately concentrated warm solution is cooled, it solidifies to a jelly-like mass. Its salts also exhibit a great tendency to crystallise in a similar manner in gelatinous masses of extremely fine needles, and are thus sharply distinguished from those of the α -acid. They contain varying amounts of water, according to the conditions under which they are formed, and are all more or less difficultly soluble in water. The *amide*, $C^{10}H^4Cl^2.SO^2(NH^2)$, crystallises from boiling alcohol in nodular aggregates of extremely fine glistening needles; it melts at about 245° , but, like the α -amide, becomes blackened (Widmann).

α -Nitronaphthalene- α -sulphonic acid, $C^{10}H^6(NO^2).SO^2H$.—This acid may be formed by nitration of naphthalene- α -sulphonic acid, and by the action of sulphuric acid on α -nitronaphthalene, but is best prepared by the latter method. It crystallises with 4 mols. of water in long straw-yellow prisms, easily soluble in pure water, but difficultly soluble in presence of sulphuric acid; hence it may be purified by precipitation with sulphuric acid. Its salts crystallise well, the *potassium* salt with half a mol. of water in large plates, the *ammonium* salt with 1.5 mol. of water in needles, and the *silver* salt in anhydrous monoclinic prisms. The *ethyl* salt melts at 101° , the chloride at 113° (Cleve, *Bull. Soc. Chim.* xxiv. 506).

By the action of sodium amalgam on its aqueous solution, α -nitronaphthalene- α -sulphonic acid is converted into sulphuric acid and amidonaphthalene (Claus a. Graeff, *ibid.* x. 1303).

The corresponding *amido-acid*, $C^{10}H^6(NH^2).SO^2H$, is a crystalline powder; on treatment with nitrous acid, it yields the *diazo-compound* $C^{10}H^6(N^2.SO^2)$, which crystallises in yellow needles, and when heated with water, is converted into a dihydroxynaphthalene, $C^{10}H^6(OH)^2$ (Cleve).

Nitronaphthalene- β -sulphonic acid.—Naphthalene- β -sulphonic acid yields, on nitration, several isomeric mononitro-derivatives, which may be partially separated by

means of the barium salts. The acid of the least soluble salt crystallises in yellow needles easily soluble in water. Its salts are mostly difficultly soluble. The *potassium* and *ammonium* salts are anhydrous; the *barium* salt contains 1 mol. of water, and is difficultly soluble, even in boiling water. The *ethyl* salt melts at 114° , the *chloride* at 125.5° .

The corresponding *amido-acid* crystallises in anhydrous rhombic plates or in prisms with 2 mol. of water (Cleve, *Bull. Soc. Chim.* [2], xxvi. 444).

The barium salt remaining after that of the above nitro-acid (Cleve's β -acid) has been separated, appears still to contain two, if not three, nitro-acids. By converting it into the chloride, extracting with hot carbon bisulphide, and crystallising the undissolved portion from carbon bisulphide, the chloride of one of these—the so-called δ -acid of Cleve—may be separated in the pure state. It crystallises in large well-defined prisms, melting at 169° , only sparingly soluble in carbon bisulphide and acetic acid. The acid formed by heating the chloride with water at 130° is easily soluble, and forms easily soluble salts. The *barium* salt, $[C^{10}H^4(NO^2).SO^3]_2Ba.H^2O$, forms pale yellow needles. The *amide*, $C^{10}H^4(NO^2).SO^2(NH^2)$, crystallises in yellow prisms melting at 216° .

The corresponding *amido-acid* crystallises from water in silvery scales (Cleve, *ibid.* xxix. 414).

Amidonaphthalenesulphonic acid. *Naphthionic acid*, $C^{10}H^4(NH^2).SO^3H$.—The acid which Piria obtained, by acting on amidonaphthalene with ammonium sulphite (iv. 17), is identical with that prepared by Schaal a. Schmidt from amidonaphthalene and sulphuric acid (Cleve, *ibid.* xxvi. 241). On displacing the NH^2 -group by Cl and distilling the resulting chloro-acid with PCl^5 , β -dichloronaphthalene is produced.

Naphthalenedisulphonic Acids.—According to Elbert a. Merz (*Ber.* ix. 592), two isomeric *naphthalenedisulphonic acids*, $C^{10}H^4(SO^3H)_2$, are simultaneously produced on heating naphthalene with an excess of sulphuric acid. About equal amounts of the α - and β -acid are formed when a mixture of 1 pt. naphthalene and 5 pts. concentrated acid is heated for four hours at 160° , the product being free from monosulpho-acid; but if the same mixture be heated for about twenty-four hours at 180° , the product consists almost entirely of the β -acid, and the pure α -acid may be converted into the β -acid by prolonged heating with sulphuric acid at 180° .

To separate the two isomerides, the hot aqueous solution is neutralised first with calcium hydrate and finally with calcium carbonate, then filtered, and the filtrate evaporated down. As the liquid becomes concentrated, crystalline crusts of the β -salt separate out, and must be removed from time to time; ultimately the concentrated solution is strained boiling hot, and then evaporated to complete dryness. If the residue thus obtained be added to boiling water, the whole of the α -salt at once dissolves, while but very little of the β -salt goes into solution; the liquid is rapidly filtered, and the filtrate left to cool in covered vessels, when almost pure α -salt is deposited. This is collected, freed from the mother-liquor by pressure, and recrystallised. A considerable amount of β -salt remains with the calcium sulphate; this is extracted by prolonged boiling with a large quantity of water, and the solution evaporated. The residue, together with the crude β -salt previously obtained, is ground up with water, and then carefully washed to remove the adhering α -salt. The calcium salts thus obtained may be converted into sodium or potassium salts in the usual manner.

By heating the dry potassium salts with phosphoric pentachloride at 140° , the corresponding sulphotchlorides are obtained in almost theoretical proportions. After distilling off the phosphoric oxychloride, the residue is treated with water, and then once or twice crystallised from boiling benzene.

α -Naphthalenedisulphonic chloride, $C^{10}H^4(SO^2Cl)_2$, crystallises from hot benzene in magnificent colourless, transparent four or six-sided plates, which may be obtained of a large size, resembling opidote crystals, by allowing the solution to evaporate spontaneously. From ether it not unfrequently crystallises in sharp needles; it is seldom obtained in well-formed crystals from an acetic acid solution. The crystals deposited from ether or acetic acid remain perfectly colourless and transparent, but those deposited from benzene generally become opaque, this change taking place either immediately or after some time; the change is in no way due to efflorescence. It dissolves in 7.5 pts. of benzene at 14° . It melts at 157° – 158° .

β -Naphthalenedisulphonic chloride crystallises from hot saturated solutions in bundles or tufts of small white needles, at most from 3–5 mm. in length. From toluene, on slow evaporation, it is deposited in large thin plates which often exhibit peculiar grotesque outlines. It dissolves in 220.7 pts. of benzene at 14° , but is much more soluble in presence of the α -chloride. It is also very slightly soluble in acetic acid, which very easily dissolves the α -chloride. It melts at 226° . Both

chlorides are decomposed and carbonised with evolution of sulphur dioxide when heated above their melting-points. When triturated with ammonium carbonate and then warmed with concentrated ammonia solution, or directly treated with the latter, they are converted into the corresponding sulphonamides. The naphthalenedisulphonic chlorides are not acted upon by sodium amalgam even at 150° (Gessner, *ibid.* ix. 1503).

α -Naphthalenedisulphonamide, $C^{10}H^6(SO^2.NH^2)^2$, is moderately soluble in hot ammoniacal water or alcohol, whereas the β -amide is very slightly soluble in the first liquid, and almost insoluble in alcohol, ether, benzene, and toluene. The α -amide crystallises in delicate glistening needles, the β -amide in small needles. The former melts at 242° – 243° ; the latter remains unfused at 305° .

By heating with water in sealed tubes at 150° , the naphthalenedisulphonic chlorides are completely converted, within three to four hours, into the corresponding acids; but if the temperature be raised to 200° , they are resolved into naphthalene and sulphuric acid. If the α -sulphonic chloride be heated with only its own volume of water, the α -sulphonic acid crystallises out on cooling in long brilliant white needles. The β -chloride cannot be entirely decomposed by so small a quantity of water at 150° – 160° , and the dilute solution obtained when the necessary amount is taken does not crystallise; but on concentrating the solution in a vacuum, it separates in small glistening white plates. Both acids are sparingly soluble in cold hydrochloric acid solution, but extremely soluble in water.

Acid salts cannot apparently be obtained from either acid. The salts of both are extremely stable; those of the α -acid contain more water than the corresponding β -salts; the water of crystallisation is, in most cases, completely expelled only above 200° . The α -salts crystallise more readily and are more soluble than the β -salts; characteristic of many of the latter is the slowness with which they dissolve.

α -Salts.—The *potassium salt*, $C^{10}H^6(SO^2K)^2.2H^2O$, crystallises from a hot saturated solution in colourless transparent needles, soluble in 1.4 pts. water at 14° . The *sodium salt*, $C^{10}H^6(SO^2Na)^2.6H^2O$, forms large glistening needles, soluble in 2.2 pts. water at 18° ; one-half the water of crystallisation is removed by exposure over sulphuric acid. The *calcium salt*, $C^{10}H^6(SO^2)^2Ca$, crystallises with varying amounts of water, separating from a rapidly cooled hot saturated solution with 3 mols., and from a slowly cooled solution with 6 mols.; the latter dissolves in 6.2 pts. water at 18° . It separates from aqueous alcohol in colourless glistening needles. The *barium salt*, $C^{10}H^6(SO^2)^2Ba.2H^2O$, forms long broad needles, soluble in 82.2 pts. water at 19° . The *lead salt*, $C^{10}H^6(SO^2)^2Pb.2H^2O$, is the most beautiful of all the α -salts, crystallising in long glistening needles, easily soluble in water.

β -Salts.—The *potassium salt*, $C^{10}H^6(SO^2K)^2$, crystallises in bushy groups of white needles, soluble in 19.2 pts. water at 18° . The *sodium salt*, $C^{10}H^6(SO^2Na)^2.H^2O$, separates in aggregates of well-formed microscopic prisms, soluble in 8.4 pts. water at 19° . The *calcium salt*, $C^{10}H^6(SO^2)^2Ca$, contains, when air-dry, from 1 to 1.5 per cent. of water. It crystallises with difficulty, and although soluble to the extent of 1 pt. in 16.2 pts. water at 18° , it is dissolved with great difficulty by water when it has been once dried. It is no more soluble in hot than in cold water, consequently a saturated solution filtered boiling hot does not deposit crystals on cooling, even after long standing. The *barium salt*, $C^{10}H^6(SO^2)^2Ba.H^2O$, closely resembles the calcium salt, but is more soluble in hot than in cold water. The *lead salt*, $C^{10}H^6(SO^2)^2Pb.OH^2$, like the calcium and barium salts, crystallises badly, and when once separated dissolves with difficulty in water.

On fusion with potassium hydrate, potassium α -naphthalenedisulphonate exchanges both sulfo-groups for hydroxyl, forming a dihydroxynaphthalene, $C^{10}H^6(OH)^2$, but the β -salt exchanges only one; the naphtholsulphonate thus produced is said to be identical with that prepared from β -naphthol and sulphuric acid.

Naphthalenetetrasulphonic Acid, $C^{10}H^4(SO^2H)^4$.—According to Senhofer (*Ber.* viii. 1486), this acid is formed on heating a solution of naphthalene in sulphuric acid with phosphoric anhydride in sealed tubes at 260° for three to four hours. Its *barium salt*, $[C^{10}H^4(SO^2)^4]Ba^2$, separates partly in ill-defined crystalline masses, and partly in long, solid, pointed prisms.

Naphthalenesulphonates. The formation of a compound of the formula $(C^{10}H^7)^2SO^2$, first observed by Berzelius in 1837 (v. 522), by the action of sulphuric acid on naphthalene, has been confirmed by Stenhouse & Groves (*Ber.* ix. 682), and also by Cleve (*ibid.* x. 1723; *Bull. Soc. Chim.*, xxv. 256). A mixture of 8 pts. pure naphthalene and 3 pts. sulphuric acid is heated to 180° in a retort. After two to three hours, water is given off, and in order to maintain the temperature constant, it is necessary to apply more heat; at this stage a reaction appears to take place, lasting one or two hours, and a considerable amount of water passes over. When, after

about another hour, water is no longer given off, the source of heat is removed, and the product allowed to cool down to 100° ; 4 pts. of boiling water are then added, and the whole poured out into a dish. When cool, the product consists of a brownish-yellow cake of the naphthalenesulphonates, mixed with excess of naphthalene, and of a pasty crystalline mass of almost pure naphthalene- β -sulphonic acid. The naphthalene is removed by steam-distillation, and the pulverised residue is then extracted with boiling carbon bisulphide and the undissolved portion washed with this solvent until the liquid runs through colourless. The solution deposits a considerable quantity of hard prismatic crystals of the α -sulphone on cooling, mixed, however, with nodular aggregates of needles, from which they may be separated either mechanically or by repeated crystallisation from alcohol and carbon bisulphide. The α -sulphone is easily purified by alternate crystallisation from these solvents, and when pure melts at 123° . The residue from the treatment of the crude product with carbon bisulphide consists almost entirely of the β -sulphone, which may be purified by recrystallisation from boiling alcohol, in which, however, it is only sparingly soluble; it crystallises in silky needles, melting at 177° (Stenhouse & Groves).

According to Cleve, the β -sulphone yields a mixture of β -chloronaphthalene and of naphthalene- β -sulphonic chloride when distilled with phosphoric pentachloride.

Mixed Sulphonates.—When a mixture of benzenesulphonic chloride, $C^6H^5.SO^2Cl$, and naphthalene, in equal molecular proportions, is heated with zinc dust, a mixed sulphone of the formula $C^6H^5.SO^2.C^{10}H^7$, melting at 121° , is produced (Crustschoff, *Ber.* vii. 1167).

According to Michael & Adair (*ibid.* x. 585), the same compound is formed, together with an isomeric (α -phenylnaphthylsulphone), on heating a mixture of benzenesulphonic acid and naphthalene with phosphoric anhydride for eight to nine hours at 170° – 190° , and is produced alone on heating a mixture of benzene and naphthalene- β -sulphonic chloride with phosphoric anhydride at 180° – 200° .

α -Naphthylphenylsulphone separates from alcohol in groups of rhombohedral crystals, melting at 100° , easily soluble in hot alcohol, ether, benzene, or acetic acid.

β -Naphthylphenylsulphone crystallises from alcohol or ether in fan-like groups of long needles, melting at 115° – 116° . The crystals are very bulky and glisten, whereas those of the α -compound are lustreless.

Dimethylamido-derivatives of these two sulphonates are obtained on heating dimethylaniline with naphthalene α - and β -sulphonic chlorides (Michler and Salathé, *Ber.* xii. 1789).

Naphthalenesulphinic Acids, $C^{10}H^7.SO^2H$. The formation of an acid of this formula from naphthalenesulphonic chloride was first indicated by Otto and Mories (vi. 860). The naphthalenesulphinic acids have more recently been studied by Gessner (*Ber.* ix. 1500).

Naphthalene- α -sulphinic acid is prepared by digesting a solution of naphthalene- α -sulphonic chloride in anhydrous ether with sodium amalgam in a flask attached to a reversed condenser. The amalgam is added gradually, finally in excess, and the heating continued until a portion of the solution leaves no residue on evaporation. The ether is then distilled off, the residue dissolved in water, the solution treated with an excess of hydrochloric acid, evaporated to a considerable extent, and then set aside to crystallise. The greater part of the acid separates in crystalline crusts. It is purified by repeated conversion into the barium salt and decomposition by sulphuric acid; finally, its solution is boiled with lead carbonate, the resulting lead salt is decomposed with sulphuretted hydrogen, and the liquid is then evaporated to the crystallising point.

It forms white glistening scales, which melt only at a high temperature, much more soluble in pure water than in water containing hydrochloric acid, moderately soluble in alcohol and sparingly soluble in ether. It is decomposed by dilute hydrochloric acid at 180° into naphthalene and sulphurous acid.

The naphthalene- α -sulphinates crystallise in glistening silky scales or needles, and are, for the most part, easily soluble in water and alcohol. The *potassium* salt, $(C^{10}H^7.SO^2K)^2.H^2O$, forms white glistening scales. The *barium* salt, $(C^{10}H^7.SO^2)^2Ba.1.5H^2O$, crystallises in fine needles, and requires 201 pts. of water at 14° and 50 pts. of boiling water to dissolve it. The *lead* salt, $(C^{10}H^7.SO^2)^2Pb.H^2O$, separates from a concentrated solution in long branched glistening needles. The *silver* salt is anhydrous, crystallising in glistening easily soluble plates which bear heating at 200° and above.

Naphthalene- β -sulphinic Acid.—Naphthalene- β -sulphonic chloride is more readily acted upon by sodium amalgam than the α -sulphonic chloride. If the product—a mixture of sodium chloride and sodium naphthalene- α -sulphinate—be extracted with alcohol, the latter is dissolved, and may readily be isolated. If the aqueous

solution of the sodium salt be treated with hydrochloric acid in excess, the sulphuric acid is precipitated as a white almost lustreless microcrystalline powder. It melts at 105° . It is by no means difficultly soluble in alcohol, ether, and pure water, but almost insoluble in dilute hydrochloric acid. It is more readily decomposed by hydrochloric acid (at 150°) than the α -acid. The *barium* salt is anhydrous, and forms white glistening needles, soluble in 16 pts. of boiling water. The *calcium* salt, $(C^{10}H^7.SO^2)Ca.3H^2O$, is a white lustreless crystalline powder, easily soluble in water and alcohol. The *magnesium* salt, $(C^{10}H^7.SO^2)Mg.6H^2O$, forms glistening scales more soluble in alcohol than in water.

Chloronaphthalenesulphinic acid, $C^{10}H^6Cl.SO^2H$, prepared by treating an ethereal solution of chloronaphthalenesulphonic bromide with sodium amalgam, &c., crystallises from alcohol in fine needles. On the addition of barium chloride to its aqueous solution, barium chloronaphthalenesulphinate, $(C^{10}H^6Cl.SO^2)^2Ba.1.5H^2O$, is gradually precipitated; by crystallisation from boiling water, it is obtained in glistening scales.

Naphthalene- α -sulphinic acid apparently yields a bromo-derivative on treatment with bromine. On adding bromine to a solution of barium naphthalene- β -sulphinate, a white precipitate of barium bromonaphthalene- β -sulphinate is at once produced (Gessner).

Naphthalenephosphonic Acids. When mercury dinaphthyl, $Hg(C^{10}H^7)^2$, is heated with phosphorous chloride, PCl^3 , in sealed tubes for several hours at 180° – 200° , two chlorides, $C^{10}H^7.PCl^2$ and $(C^{10}H^7)^2PCl$, are formed. On treatment with water, the former is converted into so-called *naphthylphosphorous acid*, $C^{10}H^7.POH(OH)$, while the latter yields so-called *dinaphthylphosphinic acid*, $(C^{10}H^7)^2.PO(OH)$, oxygen being absorbed. When the chloride $C^{10}H^7.PCl^2$ is submitted to the action of chlorine, it is converted into the tetrachloride $C^{10}H^7.PCl^4$, and this yields so-called *naphthylphosphinic acid*, $C^{10}H^7.PO(OH)^2$, on treatment with water (Kelbe, *Ber.* ix. 1051; xi. 1499). It would be more in accordance with the system adopted in the case of the sulphur acids if the derivatives of phosphoric acid were termed *phosphonic acids*, and the derivatives of phosphorous acid *phosphinic acids*, thus preserving the idea of the relationship of the former to the phosphonium type and of the latter to the phosphige type.

Naphthylphosphonic acid, $C^{10}H^7.PO(OH)^2$, crystallises in long needles, easily soluble in hot, but with difficulty in cold, water. It melts at 190° , and when heated above this temperature is converted into a glassy mass, which, on exposure to moist air, gradually regains the crystalline structure. When strongly heated, it decomposes, with separation of carbon, into metaphosphoric acid and naphthalene. The *silver* salt, $C^{10}H^7.PO(OAg)^2$, falls as a white precipitate on the addition of silver nitrate to a solution of the ammonium salt.

Dinaphthylphosphonic acid, $(C^{10}H^7)^2PO(OH)$, crystallises in needles melting at 203° ; it is insoluble in water, but easily soluble in alcohol. It decomposes carbonates.

Naphthylphosphinic acid, $C^{10}H^7.POH(OH)$, crystallises in aggregates of small white needles, difficultly soluble in cold but more soluble in hot water, almost insoluble in hydrochloric acid. When dry, it melts at 125° , but when boiled with water, it melts before dissolving.

Naphthylarsonic acid, $C^{10}H^7.AsO(OH)^2$. *Naphthylarsinic acid* (Kelbe).—This acid is prepared in the same way as the corresponding phosphonic acid, using arsenious chloride, $AsCl^3$, instead of phosphorous chloride. The former acts much more readily on mercury dinaphthyl than the latter, however. The acid crystallises from water in colourless needles, melting at 197° (Kelbe, *Ber.* xi. 1503).

Cyanonaphthalenes. α -Cyanonaphthalene is formed in by no means considerable quantity when a mixture of cyanogen gas and naphthalene vapour is passed through a tube heated to dull redness. It is also formed on passing naphthalene vapour over a mixture of potassium ferrocyanide and quartz sand heated somewhat above dull redness (Schelnberger; Merz a. Weith, *Ber.* x. 746). Another method of producing it consists in heating sulphocarbonaphthalide with copper powder (Weith, *ibid.* vi. 967).

If a solution of 2 pts. β -cyanonaphthalene in 1 pt. of alcohol be saturated with hydrochloric acid gas, it begins, after a few hours, to deposit crystals, and after twenty-four hours is converted into a solid crystalline cake of the hydrochloride of so-called β -naphthimidoethylate, $C^{10}H^7.C(NH^2Cl).OC^2H^3$ (Lohmann a. Pinner, *Ber.* xi. 1485). This compound decomposes when heated into ethyl chloride and β -naphthoic amide, $C^{10}H^7.CONH^2$. If it be agitated with an excess of ammonia solution, the free base, $C^{10}H^7.C(NH).OC^2H^3$, separates as an oil, which crystallises only after months, insoluble in water but easily soluble in alcohol, benzene, and ether. If the hydrochloride is digested with an alcoholic solution of ammonia at 50° – 60° , it is converted into the hydrochloride of the imidoamide $C^{10}H^7.N(NH)(NH^2Cl)$; this crystallises in

star-like groups of needles, easily soluble in water and alcohol, melting at 224° – 226° . The corresponding base, $C^{10}H^7.C(NH)(NH^2)$, separates as an oil on treatment of the hydrochloride with sodium hydrate solution; on exposure *in vacuo*, it solidifies to a white granular mass.

By employing isobutyl alcohol in place of ethyl alcohol, the corresponding *isobutyl* compound, $C^{10}H^7.C(NH^2Cl).OC^2H^5$, is obtained. The free base crystallises from ether in long needles melting at 38° ; on digestion with acetic anhydride, it is converted into the acetyl-derivative, $C^{10}H^7.C(NH).OC^2H^5O$, which crystallises from boiling alcohol in glistening white needles melting at 150° – 152° .

Bromo- α -cyanonaphthalene, $C^{10}H^6Br.CN$, prepared by the action of bromine on a solution of α -cyanonaphthalene in carbon bisulphide, sublimes in fine white needles melting at 147° . It is easily soluble in chloroform, benzene, boiling alcohol, ether, and glacial acetic acid (Hausmann, *ibid.* ix. 1516).

Bromo- β -cyanonaphthalene sublimes in broad white needles melting at 148° – 149° . It is easily soluble in benzene and chloroform (Hausmann).

Dicyanonaphthalenes. By distilling the pure potassium or sodium salts of the isomeric α - and β -naphthalenedisulphonic acids with potassium cyanide, Ebert & Merz (*Ber.* ix. 604) have obtained the corresponding dicyanonaphthalenes, $C^{10}H^4(CN)^2$, in a state of purity. Externally they very closely resemble each other, subliming easily and almost entirely in long white glistening needles, and crystallising in a similar manner from solvents, especially acetic acid. The α -dicyanide, however, melts at 267° – 268° , the β -dicyanide at 296° – 297° . The β -compound is almost insoluble in boiling ether, alcohol, and benzene; the α -compound is in a not inconsiderable degree soluble in boiling alcohol. By heating under pressure with hydrochloric acid at 200° – 213° , or by boiling with a solution of potassium hydrate in amyl alcohol, both are completely converted into corresponding dicarboxylic acids, but the β -compound is much the more slowly acted upon.

It is doubtful whether the dicyanonaphthalenes prepared by Darmstädter and Wichelhaus from the bromonaphthalenesulphonic acids were obtained in a state of purity.

Naphthalenecarboxylic Acids. *Naphthoic Acids*, $C^{10}H^7.COOH$. In preparing the naphthoic acids according to Merz's method, potassium ferrocyanide may with advantage be employed in place of potassium cyanide in converting the sulpho-salts into cyanides (Witt, *Ber.* vi. 488; Hausmann, *ibid.* ix. 1514).

A number of metallic salts of β -naphthoic acid have been described by Vieth (*ibid.* viii. 1278; comp. viii. 1505; ix. 1513; *Liebig's Annalen*, clxxx. 314). Both α - and β -naphthoic acid yield phthalic acid when boiled with a solution of chromic anhydride in glacial acetic acid (Vieth).

Methyl- β -naphthoate, $C^{10}H^7.COOCH^3$, produced by heating β -naphthoic chloride with methyl alcohol, forms glistening crystalline scales melting at 77° , and boiling at about 290° . The corresponding *ethyl* salt, $C^{10}H^7.COOC^2H^5$, is a very easily fusible substance; it boils at 308° – 309° (Vieth).

β -Naphthoic chloride, $C^{10}H^7.COCl$, prepared by treating β -naphthoic acid with phosphoric pentachloride, is a crystalline substance melting at 43° ; it boils at 305° (Grucarevic & Merz, *Ber.* vi. 1242; Vieth, *loc. cit.*)

β -Naphthoic amide, $C^{10}H^7.CO(NH^2)$, produced by warming the chloride with pulverised ammonium carbonate, crystallises in colourless plates, melting at 192° ; it is difficultly soluble in cold, more soluble in hot alcohol, ether, chloroform and benzene.

β -Naphthoic phenylamide, $C^{10}H^7.CO.NH(C^6H^5)$, prepared by adding the chloride in equivalent quantity to a solution of aniline in benzene, or by heating a mixture of β -naphthoic acid with an excess of aniline for several hours at 120° , forms glistening plates, easily soluble in alcohol and warm benzene and chloroform; it melts at 170° . *β -Naphthoic-tolylamide*, $C^{10}H^7.CO.NHC^7H^7$, obtained in a similar manner, forms silky glistening needles, easily soluble in alcohol and chloroform; it melts at 191° . *β -Naphthoic naphthylamide*, $C^{10}H^7.CONHC^{10}H^7$, crystallises in very small needles, difficultly soluble in ether, but moderately soluble in alcohol, chloroform, and benzene; it melts at 157° . *β -Naphthoylurea*, $C^{10}H^7.CO.N^2H^2CO$, produced by warming the chloride with urea, crystallises from hot alcohol in microscopic needles, melting at 215° (Vieth).

$\alpha\beta$ -Naphthoic anhydride, $(C^{10}H^7.CO)^2O$, is produced by heating a mixture of α -naphthoic chloride and dry potassium β -naphthoate at 150° – 160° , until the odour of the chloride has disappeared. It crystallises in fine needles melting at 126° (Hausmann, *Ber.* ix. 1515).

$\beta\beta$ -Naphthoic anhydride, $(C^{10}H^7.CO)^2O$, prepared in a similar manner from β -naphthoic chloride and potassium β -naphthoate, crystallises from ether in needles united in the form of glistening plates; it melts at 134° (Hausmann).

Naphthoylbenzoic acid, $C^{10}H^7.CO.C^6H^4.COOH$. See Ador and Crafts (*Ber.* xii. 2086).

Bromonaphthoic acids.—*Bromo- α -naphthoic acid*, $C^{10}H^6Br.COOH$, may be produced either from the corresponding cyanide (p. 1359), or by the action of bromine on silver α -naphthoate, by heating α -naphthoic acid with bromine and water at 150° – 160° , or by the action of bromine in presence of iodine on a warm acetic acid solution of α -naphthoic acid, being best prepared by the last-mentioned process. It sublimes in small white needles melting at 242° ; it is almost insoluble in boiling water, sparingly soluble in cold ether, alcohol, and acetic acid, easily soluble in benzene; from hot alcohol or acetic acid, it crystallises in granules.

In the formation of this acid from bromo- α -cyanonaphthalene, *bromo- α -naphthoic amide*, $C^{10}H^6Br.CONH^2$, is obtained as an intermediate product; it crystallises from hot alcohol in broad white needles melting at 241° .

Bromo- β -naphthoic acid is prepared in the same manner as the α -acid; the corresponding amide is also obtained as an intermediate product in its formation from bromo- β -cyanonaphthalene. The acid crystallises from alcohol or acetic acid in white granules, and sublimes in fine needles melting at 256° . It is less soluble than the α -acid.

The salts of the two acids differ considerably in solubility, the α -barium salt requiring 59 pts. and the β -salt 4300 pts. of water at 21° , while the α -calcium salt dissolves in 66.5, the β -salt in 5000 pts. of water at 20° . Both α - and β -naphthoic acid yield tetrabromo-derivatives when heated with 4–5 mols. of bromine containing some iodine, finally at a temperature of about 350° ; a portion of the acid, however, is decomposed into bromonaphthalene and carbon dioxide. By heating the β -acid with slightly more than 3 mols. of bromine containing iodine, a tribromo-derivative is produced. *Tetrabromo- α -naphthoic acid*, $C^{10}H^3Br^4.COOH$, separates from its solution in boiling alcohol or acetic acid in small granular crystals melting at 239° . The β -acid forms similar crystals melting at 260° . Both sublime with partial decomposition in needles. *Tribromo- β -naphthoic acid*, $C^{10}H^3Br^3.COOH$, melts at 270° ; it also sublimes with partial decomposition in needles (Hausmann).

Nitronaphthoic Acids.—The mononitronaphthoic acids have recently been further examined by Ekstrand (*Ber.* xii. 1393). According to this chemist, both α - and β -naphthoic acid yield two isomeric mononitro-derivatives if an excess of fuming nitric acid is added to a hot concentrated glacial acetic acid solution of either of the two, and the liquid is heated for some hours on the water bath. As the solution cools, the greater part of the less soluble modification then separates out, the more soluble modification remaining for the most part in the mother-liquor, from which it may be precipitated by the addition of water; it is most difficult, however, to separate the two modifications completely, and it is doubtful whether they have yet been obtained pure.

The less soluble *nitro- α -naphthoic acid*, after repeated recrystallisation from alcohol, forms bundles of fine pliable yellowish needles, melting at 233° , easily soluble, especially in warm alcohol, ether, acetic acid, and benzene, a hot concentrated alcoholic solution becoming almost solid on cooling. The *ethyl* salt of this acid crystallises in almost colourless long hair-fine needles melting at 92° . The *calcium* salt crystallises in hard prisms, soluble in 160 pts. of cold water.

The more soluble *nitro- α -naphthoic acid* crystallises in hard colourless prisms melting at 196° . Its *ethyl* salt forms thick hard crystals melting at 63° . The *calcium* salt forms needles or prisms soluble in 47 pts. of cold water.

To obtain the less soluble *nitro- β -naphthoic acid*, the mixture of the two acids, which could not be further separated by recrystallisation from alcohol, was digested with ether and the residue converted into calcium salt, the latter recrystallised, and then decomposed by hydrochloric acid. In this way a small quantity of an acid was obtained, difficultly soluble even in warm alcohol and acetic acid, from which it crystallised in small concentrically grouped needles, melting at about 280° . The *ethyl* salt of this modification crystallises in long glistening needles, often grouped in stars, melting at 107° . The *calcium* salt forms small plates, soluble in 930 pts. of cold water. The more soluble *nitro- β -naphthoic acid* crystallises in small needles melting at about 220° , easily soluble in warm alcohol. Its *ethyl* salt crystallises from alcohol in small needles melting at 82° . The *calcium* salt forms small needles, soluble in 388 pts. of cold water.

Sulphonaphthoic acids, $C^{10}H^6(SO^3H)(COOH)$, (Stumpf, *Liebig's Annalen*, cxxxviii. 1).— α -Naphthoic acid yields three isomeric monosulpho-acids on treatment with weak fuming sulphuric acid, that already described by Battershall being the chief product. On fusion with potassic hydrate, these furnish three corresponding *hydrosynaphthoic acids*, $C^{10}H^6(OH).COOH$, all different from the carbonaphthoic acid

of Eller and Schaeffer (vi. 852); that obtained from Battershall's sulpho-acid yields α -naphthol when distilled with lime, β -naphthol being formed when the two isomeric acids are thus treated. β -Naphthoic acid yields at most traces of an isomeric sulpho-acid, besides that described by Battershall. The corresponding hydroxy-acid furnishes α -naphthol when distilled with lime.

Naphthalenedicarboxylic Acids.—No less than four of these acids are known, viz. *naphthalic* (naphthophthalic) acid, *naphthoterephthalic* acid, and the two isomerides corresponding to the two isomeric (α - and β -) naphthalenedisulphonic acids.

Naphthalic or *Naphthophthalic* acid, $C^{10}H^6(COOH)^2$, is obtained by oxidation of acenaphthene and acenaphthylene (*ante*, p. 1345). According to Blumenthal, it is completely converted into the anhydride $C^{12}H^6O^3$ by mere exposure over sulphuric acid *in vacuo* (*Ber.* vii. 1092); the broad serrated plates, melting at 266° , obtained on subliming the acid (Behr, *Dorp.* vi. 852), appear to consist of the anhydride.

Bromonaphthophthalic acid, $C^{10}H^5Br(COOH)^2$, obtained by oxidation of bromacenaphthene, crystallises from benzene in white needles melting at 210° ; it is less readily converted into the corresponding anhydride than naphthophthalic acid on exposure over sulphuric acid. When boiled with ammonia, it yields the imide, $C^{10}H^5Br\left\{\begin{smallmatrix} CO \\ CO \end{smallmatrix}\right\}NH$, which crystallises in yellow prisms melting above 265° (Blumenthal, *loc. cit.*)

Naphthoterephthalic acid, $C^{10}H^6(COOH)^2$, obtained by boiling the dicyanonaphthalene prepared from bromonaphthalenesulphonic acid with potassic hydrate solution, crystallises in microscopic needles, which remain unfused at 240° (Wichelhaus a. Darmstädter, *Liebig's Annalen*, clii. 309).

Naphthalene- α and *β -dicarboxylic acids*, $C^{10}H^6(COOH)^2$, prepared from the dicyanonaphthalenes from naphthalene- α - and β -disulphonic acids by digestion with hydrochloric acid at 200° – 210° , or by boiling with a solution of potassic hydrate in amyl alcohol, are too difficultly soluble to be purified by recrystallisation; if dissolved in an alkali, boiled with animal charcoal, precipitated by an acid, and then well washed and dried, they are obtained as white coherent apparently amorphous masses. As prepared by decomposing the dicyanides with hydrochloric acid, the α -acid crystallises in long needles, the β -acid in short needles. The α -acid is very slightly soluble, and the β -acid almost insoluble, in boiling benzene, toluene, and acetic acid; they are somewhat more soluble in boiling alcohol. They melt far above 300° , but are decomposed. Their salts are with difficulty rendered anhydrous, some being completely dehydrated only when heated at 300° . The α -potassium salt does not crystallise; the β -salt forms large tufts of needles, very easily soluble in water, of the composition $C^{10}H^6(COOK)^2 \cdot 7\frac{1}{2}H^2O$. The α -calcium salt, $C^{10}H^6(CO^2)^2 \cdot 4OH^2$, is precipitated on the addition of calcium chloride to a neutral solution of the ammonium salt in small, often microscopic needles, but slightly soluble in water. The β -salt, $C^{10}H^6(CO^2)^2Ca \cdot 3\frac{1}{2}H^2O$, forms microscopic needles almost insoluble in water. The α - and β -silver salts are anhydrous amorphous powders which do not alter on exposure to light. Barium and zinc salts furnish white gelatinous precipitates with soluble α - and β -dicarboxylates. *Ethyl naphthalene- α -dicarboxylate*, $C^{10}H^6(COOC^2H^5)^2$, obtained by double decomposition from the silver salt and ethyl iodide, crystallises from ether in colourless needles, but is easily decomposed (Ebert a. Merz, *Ber.* ix. 606).

Hydroxynaphthalenes or Naphthols. *Dibromo- α -naphthol*, $C^{10}H^5Br^2.OH$.—To prepare this compound, bromine is added to a solution of α -naphthol in 3 pts. glacial acetic acid; it is formed even when only a single molecular proportion of bromine is employed. Crystallised from alcohol, in which it is easily soluble, it forms long glistening pliable needles, melting at 111° . It is readily and completely decomposed by an alcoholic solution of potassium hydrate, forming an easily oxidisable trihydroxynaphthalene (Biedermann, *Ber.* vi. 1119).

Bromo- β -naphthol, $C^{10}H^5Br.OH$, is obtained on adding the equivalent amount of bromine dissolved in an equal volume of glacial acetic acid to a tolerably concentrated acetic acid solution of β -naphthol. It separates in colourless needles of adamantine lustre, melting at 84° , soluble in alcohol, ether, benzene, and petroleum. It yields phthalic acid when oxidised by an alkaline solution of potassium permanganate (Smith, *Chem. Soc. J.* xxxv. 789).

Tetrabromo- β -naphthol, $C^{10}H^3Br^4.OH$.—This compound is formed by adding bromine in excess to an acetic acid solution of β -naphthol. It is less soluble than the monobromo-derivative, separating in white needles melting at 156° . When oxidised by an alkaline solution of potassium permanganate, it is converted into a monobromophthalic acid, the anhydride of which melts at 125° (Smith).

Nitronaphthols.— α -Naphthol, or the acetate formed from it, does not furnish

nitro-derivatives on nitration, but are both converted into resinous masses (Biedermann, *loc. cit.*) The nitro- α -acetamidonaphthalene, $C^{10}H^4(NO^2).NHO^2H^2O$, obtained by nitrating α -acetamidonaphthalene, however, readily exchanges the acetamido-group for hydroxyl when boiled with a concentrated aqueous solution of sodium hydrate (Andreoni a. Biedermann, *ibid.* vi. 342). The product thus obtained is a mixture of two isomeric mononitro- α -naphthols, which may be separated by extracting the mixture with cold spirit, when that of higher melting point dissolves, or better by boiling with water, as that of higher melting point is readily soluble therein, and the isomeride only slightly soluble (Liebemann a. Dittler, *Lieb's Annalen*, clxxxiii. 245).

α -Nitro- α -naphthol, $C^{10}H^4(NO^2).OH$, crystallises in very fine needles, melting at 164° , extremely soluble in alcohol and acetic acid; it is almost completely precipitated from its cold aqueous solution on the addition of a few drops of hydrochloric acid. This modification is identical with the nitronaphthol which was first obtained by Dusart, and subsequently examined by Darmstädter and Nathan (vii. 841). It yields dinitro- α -naphthol, m. p. 138° , on nitration.

Potassium α -nitro- α -naphthol, $C^{10}H^4(NO^2).OK$, forms small orange-red crystals, easily soluble in water. *Sodium α -nitro- α -naphthol*, $C^{10}H^4(NO^2).ONa.2H^2O$, crystallises in fine carmine-red needles, easily soluble in water and alcohol; the anhydrous salt is blue-red. *Barium α -nitro- α -naphthol*, $(C^{10}H^4.NO^2.O)^2Ba.H^2O$, crystallises in glistening dark-red pointed needles, exhibiting a blue dichroism; it is easily soluble in water. *Calcium α -nitro- α -naphthol*, $(C^{10}H^4.NO^2.O)^2Ca.3H^2O$, forms dark-red fine interlaced needles, easily soluble in water. *Lead α -nitro- α -naphthol*, $[C^{10}H^4(NO^2).O]^2Pb$, is a brilliant scarlet-red difficultly soluble powder. Silver α -nitro- α -naphthol is a carmine-red powder which alters on exposure to the air (Biedermann).

β -Nitro- α -naphthol forms small greenish-yellow plates, difficultly soluble in dilute alcohol and still less soluble in water; it melts at 128° . On nitration it yields the same dinitro- α -naphthol as the isomeride.

Ammonium- β -nitro- α -naphthol crystallises from a hot aqueous solution in orange-red needles; the corresponding α -nitro- α -naphthol derivative is extremely soluble, and is occasionally obtained in the form of yellowish-red star-like groups on dissolving α -nitro- α -naphthol in a very concentrated solution of ammonia. *Barium β -nitro- α -naphthol*, $(C^{10}H^4.NO^2.O)^2Ba.3OH^2$, forms glistening red needles, which become brown-red when dehydrated (Liebemann a. Dittler).

Dinitro- α -naphthol, $C^{10}H^4(NO^2)^2.OH$.—This compound is formed on boiling dinitro- α -acetamidonaphthalene with a concentrated aqueous solution of sodium hydrate. Calcium dinitro- α -naphthol crystallises either in orange-yellow needles, or in plates of the same colour, the latter form being produced when it quickly separates from concentrated solutions. This salt readily loses water on exposure over sulphuric acid (Liebemann a. Dittler).

Nitro- β -naphthol, $C^{10}H^4(NO^2).OH$.—To prepare this body, hydrated nitroso- β -naphthol is suspended in ten times its weight of water, and an equal bulk of nitric acid of sp. gr. 1.25 is then added. In the course of an hour, the pure yellow colour of the nitroso-compound changes to a yellowish-grey, and the crystals become dense and non-coherent. They are then collected, washed thoroughly with water, and treated with 50 pts. of a cold very dilute solution of sodium hydrate (1 pt. 30 per cent. solution to 50 of water) and filtered from the insoluble residue. A slight excess of acetic acid is then added to the filtrate, and the bright yellow precipitate is collected, washed, and once or twice crystallised from boiling alcohol, in which it is very soluble.

Nitro- β -naphthol thus prepared crystallises from alcohol in orange-brown plates, scarcely distinguishable from nitroso- β -naphthol. It is precipitated from its solutions as a pale-yellow crystalline powder, apparently a hydrate. It melts at 96° and forms orange-coloured, crystalline ammonium, potassium and sodium derivatives. It is more soluble than nitroso- β -naphthol, but behaves very like the latter with concentrated sulphuric and nitric acids (Stenhouse a. Groves, *Chem. Soc. J.* xxxii. 51).

Trinitro- α -naphthol, $C^{10}H^4(NO^2)^3.OH$, may be produced by digesting dinitro- α -naphthol for several hours at 30° – 50° with an excess of a mixture of equal weights of concentrated and fuming nitric acids; only from one-fifth to one-fourth of the theoretical amount is obtained, however (Ekstrand, *Ber.* x. 1232). It is more readily prepared by suspending 1 pt. of dinitro- α -naphthol in 10–15 pts. of concentrated sulphuric acid, then slowly adding, with constant stirring, to the well-cooled liquid from $1\frac{1}{4}$ – $1\frac{1}{2}$ times as much fuming nitric acid dissolved in sulphuric acid as theory requires; the mixture is left to stand surrounded with cold water for about ten days, but well agitated several times daily. It is then poured into a large quantity of ice-cold water, and the crystalline mass which separates is well washed, pressed and dried, and then recrystallised from a large quantity of boiling acetic acid. On account

of its slight solubility in the cold acid, it is readily obtained pure, and for most purposes it suffices to extract the well-pulverised dry product two or three times with boiling acetic acid or alcohol in order to remove unattacked dinitro- α -naphthol.

Trinitro- α -naphthol melts at 177°. It is a brilliant yellow dye. When oxidised by an alkaline solution of potassium permanganate, it yields nitrophthalic acid (m. p. 212°). The potassium salt has the formula $C^{10}H^4(NO_2)^3.OK.H^2O$ (Diedl a. Merz, *ibid.* xi. 1661).

Nitrobromo- α -naphthol, $C^{10}H^3Br(NO_2).OH$.—This compound is obtained by boiling the nitrobromo- α -acetamidonaphthalene formed on nitration of bromo- α -acetamidonaphthalene with a concentrated aqueous solution of sodium hydrate, &c. It closely resembles α -nitro- α -naphthol, and melts at 142° (Biedermann a. Remmers, *ibid.* vii. 538).

Nitrosonaphthols.—Two isomeric *nitroso- α -naphthols*, $C^{10}H^8(NO).OH$, are formed by the action of nitrous acid on α -naphthol, but β -naphthol yields only a single nitroso-derivative. To prepare the former, 60 grams of α -naphthol are dissolved in a dilute solution of 40 grams potassium hydrate, which is then diluted with about 18 litres of water; after cooling the liquid to 10°–5°, a solution of 70 grams potassium nitrite is added, and then, little by little, 85 grams of sulphuric acid in 1 litre of water. In a short time, a yellowish-brown flocculent precipitate is produced; after four-and-twenty hours, this is filtered off, washed and crystallised from water in order to separate a black resinous substance. By recrystallising the product thus obtained from benzene, it is separated into a more soluble yellow nitroso- α -naphthol, corresponding to β -nitro- α -naphthol, and a less soluble white isomeric corresponding to α -nitro- α -naphthol, the former being chiefly produced (Fuchs, *Ber.* viii. 626).

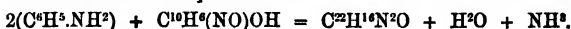
α -Nitroso- α -naphthol crystallises in dirty white or brownish coloured needles, melting with decomposition at 175°–185°; when precipitated from an alkaline solution by an acid, it has a pure white colour. It is easily soluble in acetone, alcohol and ether, but dissolves with difficulty in chloroform and carbon bisulphide, and is only sparingly soluble in hot benzene and toluene. It is oxidised with considerable difficulty by means of an excess of potassium ferricyanide in presence of alkali, and converted into α -nitro- α -naphthol (m. p. 164°); on treatment with nitric acid, it yields dinitro- α -naphthol.

β -Nitroso- α -naphthol crystallised from benzene has a yellowish-green or green colour; when precipitated from an alkaline solution, it has a pure sulphur-yellow colour. It melts, with decomposition, at 145°–150°. It is easily soluble in acetic acid, alcohol, and acetone; less soluble in benzene, carbon bisulphide, chloroform and petroleum, and almost insoluble in cold water but more soluble in hot water. It crystallises best from acetic acid, benzene or water, and in fine needles. It is a body of considerable stability, dissolving in concentrated sulphuric acid but being reprecipitated by water, being unaltered by prolonged boiling with water, being unaffected by nitrous acid in the cold, and being merely converted into the potassium-derivative by prolonged boiling with an alcoholic solution of potassium hydrate. It is somewhat volatile in a current of steam. On oxidation with potassium ferricyanide in alkaline solution, it yields β -nitro- α -naphthol (m. p. 127°). Nitric acid converts it into dinitro- α -naphthol.

Potassium β -nitroso- α -naphthol, $C^{10}H^8(NO)OK$, may be prepared either by dissolving the nitrosonaphthol in an aqueous solution of potassium hydrate, saturating the excess of the latter with carbon dioxide, evaporating to dryness, and extracting with alcohol, or by adding an alcoholic solution of potassium hydrate to an alcoholic solution of the nitrosonaphthol. In the latter case, it is precipitated in glistening metallic green plates which, when dry, appear yellowish-red in transmitted light, the superficial colour being between copper-red and bran-yellow. It is moderately soluble in water, insoluble in a solution of potassium hydrate. *Sodium β -nitroso- α -naphthol*, $C^{10}H^8(NO)ONa$, crystallises from water in glistening prisms, which appear yellow-red by transmitted light and red-brown by reflected light. *Ammonium β -nitroso- α -naphthol* is precipitated on mixing alcoholic solutions of ammonia and of the nitrosonaphthol in fine glistening metallic-green needles, which give off ammonia on exposure to the air. *Barium β -nitroso- α -naphthol*, $[C^{10}H^8(NO)O]^2Ba.2H^2O$, prepared by precipitating a solution of the nitrosonaphthol in dilute ammonia with barium chloride and recrystallising the precipitate from water, forms small glistening plates which exhibit pronounced yellowish-green and purple-red dichroism. The silver derivative is a brown-red pulverulent precipitate. The lead-derivative crystallises from alcohol in dark-brown glistening crystalline scales. The *methyl* derivative, $C^{10}H^8(NO).OCH^3$, prepared from the silver-derivative, crystallises from dilute alcohol in yellowish-green to steel-blue coloured needles, melting at 95°. The *ethyl* derivative crystallises in very thin, flat, glistening, greenish-yellow needles, melting at 101°. *Benzoyl β -nitroso- α -naphthol*, $C^{10}H^8(NO)O.CO.C^6H^5$, is produced by adding the sodium derivative to

cooled benzoic chloride. The semi-solid mass is heated for a few moments on the water bath, then digested with cold water for three to four hours, the benzoic acid extracted by boiling with water and alcohol, and the residue crystallised from a mixture of acetone and chloroform. It crystallises in short thick yellow needles, which decompose at 140° – 150° into benzoic acid and a black residue.

β -nitroso- α -naphthol appears to combine with bromine, forming a dibromide, $C^{10}H^6Br^2(NO).OH$, which crystallises in glistening silver-white plates, melting at 145° . On adding β -nitroso- α -naphthol to an alcoholic solution of aniline, long yellow needles of an extremely unstable body are obtained, probably a compound of the two substances. If, however, aniline be added to a solution of the nitrosonaphthol in acetic acid, and the liquid be then warmed on the warm bath, it gradually darkens in colour and finally becomes violet; on then pouring it into water, a solid dark-red product separates. After washing this with water, and extracting first with hot dilute ammonia, then with hot alcohol, a residue remains, which crystallises from a mixture of alcohol and benzene in fine needles, exhibiting while suspended in the liquid a magnificent cantharides-like lustre. This substance dissolves in acids forming magnificent violet-coloured solutions, from which it separates, on the addition of ammonia, as an orange-coloured precipitate. It has the composition $C^{22}H^{16}N^2O$, and is apparently formed in accordance with the equation:



Methyl and ethyl nitrosonaphthol behave in a similar manner with aniline, and a precisely similar product is obtained from paratoluidine (Fuchs, *ibid.* viii. 1022).

Nitroso- β -naphthol, $C^{10}H^6(NO).OH$.—This compound was first obtained by Fuchs (*ibid.* 1026). According to Stenhouse a. Groves (*Chem. Soc. J.* xxxii. 47), the following is the most advantageous method of preparing it: 1 pt. of β -naphthol is dissolved in 10 pts. boiling water by means of 1 pt. by measure of a solution of sodium hydrate of sp. gr. 1.323 (a 30 per cent. solution); the liquid is then cooled and added to 100 pts. of water. This solution is at once mixed, with constant stirring, with a nitrating solution prepared by pouring 2 pts. by weight of a 15 per cent. solution of the compound $SO^2(NO^2).OH$ (*ibid.* xxxi. 545) into 200 of water. After standing for twelve to twenty hours, the precipitate of crude nitroso- β -naphthol which forms is collected on a linen filter and washed until the washings are no longer acid. The purification of this product is based on the insolubility of the barium-derivative, which is thrown down as a bulky green precipitate on the addition of barium chloride to a solution of the nitrosonaphthol in dilute alkali, and on the insolubility of the sodium-derivative even in comparatively dilute solutions of sodium hydrate. Sufficient water is added to the paste from the filter to make it up to 35 pts. by measure; 1 pt. of the 30 per cent. solution of sodium hydrate diluted with 35 of water is then added, and the mixture agitated occasionally and filtered after standing about an hour. The clear filtrate is precipitated by a slight excess of a dilute solution of barium chloride—about 1.5 pts. of a cold saturated solution diluted with twice its weight of water—and the green precipitate collected on a fine cambric filter. After being thoroughly washed, it is suspended in about 35 pts. of water, and decomposed with hydrochloric acid in excess. The partially purified nitroso-compound is then washed until free from barium chloride, suspended in 15 pts. of water, and heated on the water bath with 5 pts. of 30 per cent. sodium hydrate solution; to the filtered liquid, one-tenth of its bulk of soda solution is then added: this causes the precipitation of the sodium nitroso- β -naphthol, which is collected, pressed, and decomposed by acid, the process of precipitation as sodium compound being repeated if necessary.

In this way, nitroso- β -naphthol is obtained in minute needles of a brilliant yellow colour, containing water of crystallisation, and becoming brown at a gentle heat, owing to loss of water. The anhydrous compound crystallises from alcohol, &c., in thin plates or short thick prisms of an orange-brown colour, melting at $109^{\circ}.5$. It is only slightly soluble in water, even when boiling, but dissolves readily in benzene, carbon bisulphide, acetic acid and hot alcohol; it is comparatively slightly soluble in light petroleum, even when boiling. It dissolves in cold concentrated sulphuric acid, forming a bright-red liquid, from which it is precipitated unaltered by water; on strongly heating the acid solution, the colour changes to brown, and water then no longer has any effect. It yields nitro- β -naphthol and a body insoluble in dilute alkaline solutions on careful treatment with dilute nitric acid; if alcohol be used instead of water, a somewhat different reaction appears to take place; concentrated nitric acid forms tarry products.

The ammonium and alkali metal derivatives of nitroso- β -naphthol are crystalline and of a bright green colour when in a finely divided state, although the masses of crystals deposited from a hot concentrated solution appear black by reflected light. The alkaline earth-metal derivatives are also of various shades of green.

Amidonaphthols. *α -Amido- α -naphthol*, $C^{10}H^6(NH^2).OH$.—This compound is formed on reduction of α -nitro- α -naphthol. To prepare it, the latter body is digested with tin and hydrochloric acid; the white crystals of the tin double salt which are then obtained are dissolved in water; the tin separated by means of hydrogen sulphide; and the solution concentrated out of contact with the air. On addition of hydrochloric acid to the concentrated liquid, α -amido- α -naphthol hydrochloride crystallises out in white needles or elongated needle-like plates, very easily soluble in water. It yields almost the theoretical amount of α -naphthaquinone on treatment with a variety of oxidising agents. On the addition of bromine water, even to very dilute solutions, a precipitate of yellowish-white needles is formed; this contains both nitrogen and bromine, and probably corresponds to the compound obtained by Schmitt a. Bennewitz from paramidophenol and chloride of lime (Liebermann a. Dittler, *Liebig's Annalen*, clxxxiii. 247).

β -Amido- α -naphthol.—The hydrochloride of this compound, obtained in a similar manner to the above from β -nitro- α -naphthol, crystallises in broad white plates. On the addition of alkali and agitation with air, its aqueous solution acquires a permanent grass-green colour, and after a time a green scum separates, which dissolves in alcohol to form a pure green-coloured liquid. The α -compound, when similarly treated, first exhibits a dirty-green coloration, which soon passes into yellow. It furnishes a yellowish to green precipitate with bromine water or ferric chloride, but no naphthaquinone is formed on heating (Liebermann a. Dittler).

Nitroso- β -naphthol appears to be converted on reduction into the corresponding amido-derivative, but this has not yet been examined (comp. β -naphthaquinone).

Triamido- α -naphthol, $C^{10}H^4(NH^2)^3.OH$.—This compound has not yet been isolated, but its sulphate and the tin double salt of its hydrochloride are known (Diehl a. Merz, *Ber.* xi. 1663). To prepare the latter, 8 pts. of the strongest hydrochloric acid are poured on a mixture of 1 pt. trinitro- α -naphthol and 4 pts. granulated tin, and heat is then carefully applied; a violent reaction soon takes place, and a clear brown solution is formed. When sufficiently concentrated, this deposits granules of prismatic crystals having the formula $C^{10}H^4(NH^2Cl)^3.OH, SnCl_2.H^2O$ (Eckstrand). If the solution of this salt be freed from tin by means of hydrogen sulphide and then sufficiently concentrated in a current of the gas, it deposits fine white needles of triamidonaphthol hydrochloride, but this salt is extremely unstable, and rapidly undergoes oxidation even when dry. The sulphate, $C^{10}H^4(NH^2)^3.OH, H^2SO_4.H^2O$, however, is more stable; it separates on addition of sulphuric acid to the very concentrated warm solution of the hydrochloride on cooling in yellow crystalline crusts, easily soluble in water. The dry salt is moderately stable in the air, but its solution rapidly assumes a red colour on agitation with air, and is immediately reddened by ferric chloride.

Dihydroxynaphthalenes, $C^{10}H^6(OH)^2$.—Four of these are known, viz.: 1. α -naphthaquinol or α -naphthahydroquinone (vii. 836); 2. β -naphthaquinol or β -naphthahydroquinone; 3. that derived from α -nitronaphthalene- α -sulphonic acid; and 4. that formed by fusing naphthalene- α -disulphonic acid with alkali. The last of these was first obtained, but in an impure state, by Dusart, and was subsequently examined by Darmstädter a. Wichelhaus (vi. 857); the pure substance has more recently been described by Ebert a. Merz.

β -Naphthaquinol, produced by the action of hydriodic acid or of sulphurous acid on β -naphthaquinone, crystallises in colourless needles. When alcoholic solutions of β -naphthaquinone and β -naphthaquinol are mixed, water added, and the liquid gently heated, dark-coloured crystals are deposited, resembling those obtained from the corresponding α -compounds under similar circumstances (Stenhouse a. Groves, *Chem. Soc. J.* xxxii. 53).

Dihydroxynaphthalene, prepared by heating potassium naphthalene α -disulphonate with potassium hydrate at 280° – 300° , crystallises from boiling benzene in long colourless needles, melting at 186° . It sublimes with partial decomposition in broad toothed plates; it scarcely volatilises with vapour of water. It is easily soluble in boiling water, and still more so in alcohol and ether; moderately soluble in benzene, toluene, and chloroform, and almost insoluble in carbon bisulphide and petroleum. An alkaline solution darkens rapidly on exposure to the air, and an ethereal solution behaves similarly. Its aqueous solution is coloured red temporarily by chloride of lime and more permanently by nitric acid. It appears to yield isomeric nitro- and haloïd-derivatives (Ebert a. Merz, *Ber.* ix. 609; Weber, *ibid.* x. 1233).

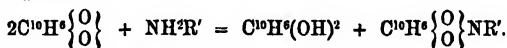
According to Cleve (*Bull. Soc. Chim.* xxiv. 513), the amido-acid formed on reduction of nitronaphthalene- α -sulphonic acid yields by Griess's method a dihydroxynaphthalene subliming in needles which do not fuse below 220° .

Dinaphthols.—According to Dianin (*ibid.* viii. 166), β -dinaphthol yields the compound $C^{20}H^{12}O$ when distilled with phosphoric pentoxide. This body crystallises in long yellow needles; it combines with a single molecular proportion of trinitrophenol.

Dinaphthyl- β -diquinol, $C^{20}H^{14}(OH)^4$.—This compound is formed by the reduction of β -dinaphthylidiquinone or the corresponding quinhydrone. When the diquinone is allowed to stand for some time in contact with sulphurous acid solution, it becomes converted into a mass of colourless crystals, apparently without the quinhydrone being formed as an intermediate product. A very convenient method of preparation is to convert β -naphthaquinone into the diquinhydrone by treatment with dilute sulphuric acid, and when the mixture is cold, to add about twice its bulk of a saturated aqueous solution of sulphurous acid; when the whole has stood about twenty-four hours, the black diquinhydrone will be found to have been entirely converted into a mass of snow-white needles of the diquinol, provided the β -naphthaquinone originally employed was quite pure; these merely require to be thoroughly washed to remove sulphuric acid, and crystallised once from dilute acetic acid to which a few drops of sulphurous acid solution have been added to be quite pure.

Dinaphthyl- β -diquinol forms colourless needles, which on drying become darkened from partial oxidation. It melts at 176° – 178° , is almost insoluble in water, moderately soluble in 30 per cent. acetic acid, easily in glacial acetic acid; it is only slightly soluble in benzene, carbon bisulphide and ether (Stenhouse a. Groves, *Chem. Soc. J.* xxxiii. 419).

Naphthaquinones. Monnet, Reverdin and Nölting (*Ber.* xii. 2305) have obtained α -naphthaquinone by direct oxidation of α -amidonaphthalene (naphthylamine), and also in small quantity by oxidation of naphthionic acid. 1 pt. naphthylamine was dissolved in 6 pts. sulphuric acid and 25 pts. water, and 2.5 pts. of finely pulverised potassium dichromate were then added gradually to the cooled solution; the resulting dark-brown precipitate was filtered off, dried over sulphuric acid, and extracted with ether, and the mother-liquor also extracted with ether. In one experiment, 40 per cent., in others only 15–20 per cent., α -naphthaquinone was obtained in this way; a variable amount of phthalic acid and a brown substance insoluble in almost all solvents are also formed. α -Naphthaquinone reacts with dimethylaniline, phenol, and resorcinol in presence of sulphuric acid to form coloured substances, which appear, however, to be of no technical value. According to Plimpton and Zincke (*Ber.* xii. 1644), it readily enters into reaction with primary monamines apparently in accordance with the equation:



The compounds obtained with aniline, paratoluidine and methylamine crystallise in beautiful red needles melting at 191° , 200° , and 225° respectively.

Dibromo- α -naphthaquinone, $C^{10}H^6Br^2O^2$, is produced by treating α -naphthol with iodine and an excess of bromine (Diehl a. Morz, *ibid.* x. 1066). α -Naphthol is mixed with double its weight of iodine and a considerable quantity of water and seven times its weight of bromine is then gradually added. This mixture is heated in a vessel attached to a reversed condenser for several hours. The product is boiled with a large quantity of alcohol or acetic acid, and the crystals which separate are purified by recrystallisation. It may also be obtained by treating dinitro- α -naphthol in a similar manner; in either case, about 50 per cent. of the theoretical amount is formed.

Dibromo- α -naphthaquinone crystallises in small granules consisting of hair-fine needles; when carefully heated, it sublimes with partial decomposition in yellow needles, melting at $151^{\circ}.5$. It is sparingly soluble in acetic acid, alcohol, benzene, and ether, but readily soluble in boiling alcohol or acetic acid.

β -Naphthaquinone, $C^{10}H^6O^2$ (Stenhouse a. Groves, *Chem. Soc. J.* xxxii. 47, xxxiii. 415).—This compound is produced by oxidation of the amidonaphthol formed on reduction of nitroso- β -naphthol. To prepare it, nitroso- β -naphthol is first converted into the barium-derivative by dissolving it (2 pts.) in a mixture of about 100 pts. water with 2 pts. 30 per cent. sodium hydrate solution, filtering, then adding a slight excess of barium chloride. The precipitate, after being collected and washed, is suspended in 140 pts. water, mixed with 3 pts. ammonia solution (sp. gr. 880), and the liquid supersaturated with hydrogen sulphide. The vessel containing the mixture is then tightly corked and allowed to stand several hours; subsequently, the precipitate is collected, washed with a very dilute solution of hydrogen sulphide, then added to 6 pts. of a saturated aqueous solution of sulphurous acid and 6 pts. of dilute sulphuric acid (1 vol. acid to 2 vols. water), the liquid filtered, and the filtrate immediately poured into a filtered solution of 3 pts. potassium dichromate in 20 pts. of water.

The quinone at once separates in slender needles of a bright orange colour. It is collected without delay, thoroughly washed with distilled water, and dried at the ordinary temperature; thus prepared, it is pure with the exception that it contains traces of chromium, which, however, cannot be removed by crystallisation from any solvent, as it decomposes very readily. Only from 62–65 per cent. of the weight of the nitrosonaphthol, instead of 91.9 per cent., is thus obtained, however.

β -naphthaquinone melts at 96° . If boiled for some time with dilute nitric acid, it is oxidised to phthalic acid.

Nitro- β -naphthaquinone, $C^{10}H^5(NO^2)O^2$.— β -Naphthaquinone dissolves readily in hot dilute nitric acid, and the solution on cooling deposits magnificent crimson-coloured needles of nitro- β -naphthaquinone. The latter may be prepared by adding 10 pts. of the quinone to 60 pts. by measure of nitric acid (of sp. gr. 1.2), agitating until a homogeneous paste is formed, and then plunging the flask into boiling water for a few minutes; the quinone dissolves, but very shortly afterwards a mass of crystals of the nitro-derivative separate out. When the conversion is complete, the flask is cooled, and after a couple of hours the product is collected and washed; it is then recrystallised from boiling benzene, and afterwards once or twice from boiling glacial acetic acid. From the latter solvent, it crystallises in magnificent crimson plates bearing a striking resemblance in point of colour and general aspect to chromic anhydride. It melts at 158° . It is insoluble in light petroleum, almost insoluble in carbon bisulphide, slightly soluble in ether, more so in benzene and in boiling alcohol, and very readily soluble in hot glacial acetic acid; boiling with alcohol, however, appears to decompose it.

Dinaphthyl- β -diquinone, $C^{20}H^{10}O^4$ (Stenhouse & Groves, *Chem. Soc. J.* xxxiii. 416).—When β -naphthaquinone (1 pt.) is intimately mixed with dilute sulphuric acid (10 pts. by measure of 1 vol. acid to 2 vols. water) so as not to leave any part unwetted, and allowed to remain in contact therewith for twenty-four hours, it is completely converted into its own weight of a compound which is analogous to quinhydrone, and in all probability has the formula $C^{20}H^{14}O^8$; the same change may be more rapidly effected by heating the mixture at about 55° . The product merely requires thorough washing with cold water.

Dinaphthyl- β -diquinhydrone is an indigo-black powder when dry, insoluble in water, carbon disulphide, and light petroleum, almost insoluble in benzene, but soluble in glacial acetic acid. By boiling with nitric acid, or with a solution of potassium dichromate and sulphuric acid, it is converted into dinaphthyl- β -diquinone, $C^{20}H^{10}O^4$. This compound is most conveniently prepared by pouring a solution of pure dinaphthyl- β -diquinol, $C^{20}H^{10}(OH)^4$, in boiling 30 per cent. acid into sufficient nitric acid (sp. gr. 1.45) to oxidise it. It is then precipitated in small lustrous prisms of a brilliant orange colour. Dinaphthyl- β -diquinone is but very slightly soluble, or insoluble, in all ordinary solvents; it is a very stable body, dissolving in boiling concentrated nitric acid, and crystallising out unchanged on cooling. It is also easily soluble in warm concentrated sulphuric acid, and is precipitated again on dilution.

Hydroxy- α -naphthaquinone or *Naphthalic acid*, $C^{10}H^5(OH)O^2$.—This compound, which is usually prepared by heating diimidonaphthol hydrochloride with hydrochloric acid at 120° in sealed tubes (vii. 836), is more readily prepared, according to Merz & Diehl (*Ber.* xi. 1314) by adding the finely pulverised hydrochloride little by little to a moderately concentrated boiling solution of sodium carbonate; the product obtained on acidifying the filtered solution is sufficiently pure for most purposes. An insoluble dark-coloured substance is also formed in varying amount according to the purity of the hydrochloride employed. It is well to operate quickly and on a small scale, so as to avoid access of air as much as possible; using 40 to 60 grams of hydrochloride, from 75 to over 80 per cent. of the theoretical amount is obtained. Hydroxy- α -naphthaquinone is also formed on heating diamido- α -naphthol with dilute hydroxylic acid at 180° . Carefully crystallised hydroxy- α -naphthaquinone melts at 179° . If heated with an aqueous or alcoholic solution of ammonia at 100° – 110° , it is converted into amidonaphthaquinone (Ludwig, *ibid.* iv. 970).

Bromohydroxy- α -naphthaquinone or *Bromonaphthalic acid*, $C^{10}H^4Br(OH)O^2$, is produced on treatment of dibromo- α -naphthaquinone, $C^{10}H^4Br^2O^2$, with a warm solution of sodium hydrate or with a boiling solution of sodium carbonate, and by the action of bromine on hydroxy- α -naphthaquinone (Diehl & Merz, *ibid.* xi. 1066). It crystallises from hot alcohol in compact almost golden-yellow plates, melting at 196° – 5 .

The potassium derivative, $C^{10}H^4BrO^2K \cdot 4H^2O$, crystallises in granular masses of small dark-red needles, very soluble in water. The barium derivative, $(C^{10}H^4BrO^2)^2Ba$, is obtained as an orange-coloured precipitate on the addition of barium chloride to a

cold solution of the potassium derivative. Other metallic salts also produce coloured precipitates. Bromohydroxy- α -naphthaquinone yields phthalic acid on oxidation with nitric acid.

Nitrohydroxy- α -naphthaquinone or *Nitronaphthalic acid*, $C^{10}H^4(NO^2)(OH)O^2$.—The nitration of hydroxy- α -naphthaquinone presents difficulties, but may be effected by dissolving it in 10 pts. concentrated sulphuric acid and gradually adding the required amount of fuming nitric acid. The solution is left at rest for forty-eight hours, care being taken to keep it cool, and then poured into ice water. The product is collected, washed with ice-water, pressed and crystallised alternately from dilute alcohol and chloroform (Merz a. Diehl, *ibid.* xi. 1314).

Nitrohydroxy- α -naphthaquinone crystallises from hot chloroform in pale yellow plates or scales; from benzene it separates in large thin plates like crystals of sublimed naphthalene. It is easily soluble in hot water, alcohol, and ether, sparingly soluble in cold benzene, chloroform, or petroleum, and not very soluble in the hot liquids. It melts with decomposition at 157° ; it also decomposes if heated for some time at 140° , hydrocyanic acid being one of the products. Its aqueous solution is entirely decomposed by prolonged boiling, hydrocyanic acid, much humus-like substance and a considerable amount of phthalic acid being produced. It is easily oxidised by hot dilute nitric acid and converted into phthalic acid.

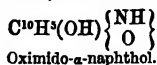
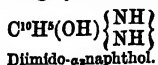
The potassium derivative, $C^{10}H^4O^2(NO^2)(OK)$, crystallises in bundles of golden-yellow glistening needles, sparingly soluble in cold, easily in hot water. The barium derivative, $[C^{10}H^4O^2(NO^2).O]^2Ba$, crystallises from a hot solution in orange-red scales, very slightly soluble in water. The lead derivative crystallises according to circumstances in one or other of two modifications differing in the amount of water of crystallisation and solubility; it adheres in a remarkable manner to lead carbonate, and notwithstanding its solubility is with difficulty separated from the latter by boiling water.

Amidohydroxy- α -naphthaquinone or *Amidonaphthalic acid*, $C^{10}H^4O^2(NH^2)(OH)$, is produced by reduction of the foregoing compound, either by means of tin and hydrochloric acid or ammonium sulphhydrate (Merz a. Diehl). It crystallises from hot glacial acetic acid or alcohol in loosely aggregated dark-brown needles, moderately soluble in hot glacial acetic acid and alcohol, but sparingly in cold. It dissolves in solutions of ammonia and ammonium carbonate, and of the hydrates and carbonates of the alkali-metals, forming intense blue coloured liquids resembling an ammoniacal solution of a cupric salt; its alkaline earth and heavy metal derivatives are difficultly soluble or insoluble. It also exhibits basic properties, solutions of its metallic derivatives being precipitated by acetic but not by hydrochloric or sulphuric acids.

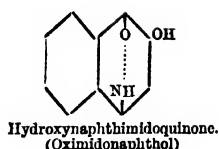
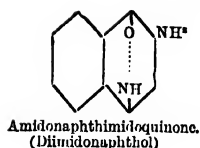
It is readily oxidised by nitric acid and converted into phthalic acid. When heated for 1-1½ hours at 170° - 180° with dilute hydrochloric acid, it is converted into *dihydroxy- α -naphthaquinone*, $C^{10}H^4O^2(OH)^2$. The latter crystallises from alcohol in fine red-brown needles, and from glacial acetic acid in dark-red plates; the crystals exhibit a brilliant metallic lustre in sunlight. It is abundantly soluble in hot alcohol and glacial acetic acid, although somewhat sparingly in the cold liquids; it is only slightly soluble in benzene and ether; it may be dissolved in a large quantity of water, but as the solution cools separates almost entirely in fine needles. A solution of the freshly precipitated substance in ammonia and alkalis has a dark violet-blue colour, similar to that of the higher methylated rosanilines. If somewhat rapidly heated it sublimes in bundles of vermilion-red needles, but much of it undergoes decomposition. The metallic derivatives of dihydroxy- α -naphthaquinone are all dark-coloured, and excepting those of the alkali-metals are only slightly soluble or insoluble. With alumina mordants it dyes violet, and with iron mordants dark-blue, and the colour withstands washing. It communicates to silk a brownish-violet colour and strong metallic lustre. It is dissolved on treatment with tin and hydrochloric acid, and apparently converted into *tetrahydroxynaphthalene*, $C^{10}H^4(OH)^4$.

Diacetoxy- α -naphthaquinone, $C^{10}H^4O^2(OC^2H^3O)^2$, produced by heating dihydroxy- α -naphthaquinone with an excess of acetic anhydride at about 160° for one to two hours, crystallises from hot dilute alcohol in small brown plates.

Diimido- and Oximido- α -naphthol.—These compounds have been represented by Graebe a. Ludwig by the following formulæ (vii. 841):



It appears probable, however, that both are derivatives of an 'imidoquinone,' intermediate in composition between naphthaquinone and the at present unknown diimido-naphthalene, so-called diimidonaphthol being *amido-* and oximidonaphthol *hydroxy-naphthimidoquinone*, thus:



The fact that the so-called diimidonaphthol unites with a single molecule of hydrochloric acid, and that oximidonaphthol is precipitated as such on the addition of hydrochloric acid to its solution in concentrated alkali, obviously supports this view.

Amidodiimido- α -naphthol.—According to Diehl a. Merz, the hydrochloride of this compound is produced on adding a slight excess of ferric chloride to a hot solution of triamidonaphthol hydrochloride, $C^{10}H^4(NH^2Cl)^3.OH$. It crystallises in lustrous dark-green plates, moderately soluble in cold water and alcohol, very sparingly in ether and concentrated hydrochloric acid. Its solutions are of an intense dark-red colour, and colour wool a brown-red and silk a similar but somewhat redder shade. Its aqueous solution is decomposed on prolonged boiling, and even the dry substance is not permanent.

On the addition of potassium dichromate to a solution of the hydrochloride, $C^{10}H^4N^3O.HCl$, the chromate, $C^{10}H^4N^3O.H^2CrO_4$, is thrown down as a flocculent or pulverulent brown-red precipitate. The platino-chloride, $(C^{10}H^4N^3O.HCl)^2PtCl_4$, is precipitated on the addition of platinum chloride to a solution of the hydrochloride as a dark-brown precipitate almost insoluble in water. The amidodiimidonaphthol itself, $C^{10}H^4N^3O$, is thrown down on the addition of alkali to a solution of the hydrochloride in brown-red flocculi consisting of extremely fine needles. It crystallises from hot alcohol in dark-brown needles, abundantly soluble in hot, but moderately in cold alcohol, and very slightly soluble in cold benzene, ether, and water.

It may be questioned whether the compound thus obtained is really an amidodiimidonaphthol of the formula $C^{10}H^4(N^2H^2)(NH^2)(OH)$, as Diehl a. Merz suppose, and whether it is not a diamidoimidoquinone, i.e. the amido-derivative of the so-called diimidonaphthol of Graebe a. Ludwig.

Amidonaphthalenes. β -Amidonaphthalene or β -Naphthylamine, $C^{10}H^7.NH^2$, the isomeride of ordinary α -amidonaphthalene, or α -naphthylamine, is produced on reduction of the bromonitronaphthalene obtained by brominating α -acetamidonaphthalene, nitrating the resulting bromo- α -acetamidonaphthalene, converting the nitrobromo-compound thus produced into nitrobromonaphthylamine, and finally displacing the amido-group in this latter compound by hydrogen by Griess's method (Liebermann a. Scheiding, *Liebigs Annalen*, clxxxiii. 258).

β -Amidonaphthalene volatilises in a current of steam; it crystallises from water in snow-white glistening plates melting at 112° . It is readily distinguished from the isomeride by failing to yield a coloration either with ferric chloride or with chromic acid, with bleaching powder, or alcohol containing nitrous acid and a little hydrochloric acid; it also has not the characteristic odour of α -naphthylamine. Its aqueous solution exhibits a blue fluorescence, but solutions of its salts are not fluorescent.

β -Naphthylammonium chloride, $C^{10}H^7.NH^2Cl$, forms colourless plates, very easily soluble in water and alcohol, difficultly soluble in dilute hydrochloric acid. The platinochloride, $(C^{10}H^7.NH^2Cl)^2PtCl_4$, forms yellow plates soluble in water. β -Naphthylammonium sulphate, $(C^{10}H^7.NH^2)^2SO_4$, crystallises from hot water in colourless plates; it is precipitated on the addition of sulphuric acid to a cold dilute solution of the hydrochloride, and as it is much less soluble than the α -naphthylamine salt, the two isomerides may be separated by means of their sulphates. β -Naphthylamine combines with trinitrophenol, forming a trinitrophenate, which crystallises in long yellow needles melting at 195° , easily soluble in alcohol.

β -Acetamidonaphthalene or β -acenaphthalide, $C^{10}H^7.NHC^2H^3O$, crystallises from water in elongated glistening plates, melting at 132° .

α -Amidonaphthalene. Reactions.—If a small quantity of an alcoholic solution of nitrous acid be mixed with a solution of α -naphthylamine in alcohol or glacial acetic acid and a little hydrochloric acid be then added, an intense violet to magenta coloration is produced if a considerable quantity of the base be present; if only a trace of the base be present, the liquid acquires a reddish colour (Liebermann).

An extremely delicate test for nitrous acid consists in adding to the suspected solution acidulated with pure sulphuric acid, a little sulphanilic acid, and about ten

minutes afterwards a few drops of a colourless solution of naphthylammonium sulphate; a more or less magenta-red colour is thus produced (Griess, *Ber.* xii. 426).

α -Naphthylamine forms a crystalline compound with mercuric chloride (O. Klein, *Ber.* xi. 743). It enters into reaction with dinitrochlorobenzene, especially on warming in an alcoholic solution of the two bodies, but the product is not a well-characterised substance (Laubenheimer, *ibid.* xi. 1158).

When heated together in sealed tubes for three to four hours at 190° – 220° , naphthylamine hydrochloride and nitronaphthalene enter into reaction in accordance with the equation, $2(\text{C}^{10}\text{H}^7\text{NH}_2) + \text{C}^{10}\text{H}_7\text{NO}_2 = \text{NH}_3 + 2\text{H}_2\text{O} + \text{C}^{20}\text{H}^{14}\text{N}_2$, forming trinaphthylenediamine (Salzmann a. Wichelhaus, *ibid.* ix. 1107).

If α -naphthylamine be heated with rather less than half its weight of urea at 120° for some hours, *dinaphthylcarbamide*, $(\text{C}^{10}\text{H}^7\text{NH})_2\text{CO}$, is the sole product; but *mononaphthylcarbamide*, $\text{NH}_2\text{CO.NH.C}^{10}\text{H}^7$, is also formed on heating naphthylamine hydrochloride with urea at 150° – 170° (Pagliani, *Gazz. chim. ital.* ix. 28).

Methyl- α -naphthylamine, $\text{C}^{10}\text{H}^7\text{NH}(\text{CH}_3)$, is produced, together with dinaphthylamine, $\text{NH}(\text{C}^{10}\text{H}^7)_2$, on passing a current of methyl chloride gas into α -naphthylamine heated at about 150° – 180° (Landshoff, *Ber.* xi. 638). The former boils at 293° . It rapidly becomes dark-coloured and untransparent on exposure to the air; its alcoholic solution yields a dark violet precipitate with ferric chloride. The monoacetyl-derivative crystallises from water in small white prisms melting at 91° ; although difficultly soluble in water, it separates very slowly from an aqueous solution.

Dimethyl- α -naphthylamine, $\text{C}^{10}\text{H}^7\text{N}(\text{CH}_3)_2$, is produced in theoretical amount on heating a mixture of 1 mol. proportion of naphthylamine dissolved in methyl alcohol and 2 mol. proportions of methyl iodide in closed tubes at 170° during one day. It is a pale-yellow strongly refracting oil, having an odour like that of petroleum, boiling at 267° ; it exhibits an intense green fluorescence. On the addition of ferric chloride to its alcoholic solution, a violet coloration is produced, which passes into a beautiful violet on exposure to the air.

Trimethylnaphthylammonium iodide, $\text{C}^{10}\text{H}^7\text{N}(\text{CH}_3)_3\text{I}$, formed by combining dimethylnaphthylamine with methyl iodide, crystallises from water in large slightly yellowish-green coloured needles, easily soluble in hot and cold water. At 164° it splits up into methyl iodide and dimethylnaphthylamine. It is not altered by sodium hydrate, but on digestion with silver hydrate is converted into the hydroxide, $\text{C}^{10}\text{H}^7\text{N}(\text{CH}_3)_3(\text{OH})$.

Ethyl- α -naphthylamine, $\text{C}^{10}\text{H}^7\text{NH}(\text{C}_2\text{H}_5)$, is formed on reduction of α -thiacetamidonaphthalene (Bernthsen a. Trompeter, *Ber.* xi. 1756).

Dinaphthylamine, $\text{NH}(\text{C}^{10}\text{H}^7)_2$.—On the addition of potassium nitrite to an acetic acid solution of this base, *nitrosodinaphthylamine*, $\text{N}(\text{C}^{10}\text{H}^7)_2(\text{NO})$, separates as a yellow oil which soon becomes solid. The product is dissolved in as little benzene as possible, and the solution then precipitated with dilute alcohol. It forms a crystalline powder, melting with decomposition at 260° – 262° (Landshoff, *Ber.* xi. 641).

α -Thiacetamidonaphthalene, $\text{C}^{10}\text{H}^7\text{NH}(\text{CS.CH}_3)$.—This body, termed by Bernthsen a. Trompeter acetonaphthylthianide, is obtained on heating the amidine $\text{CH}_3\text{C}(\text{NH})_2\text{NH.C}^{10}\text{H}^7$ (viii. 71) with carbon bisulphide for several hours at 100° . It crystallises in yellowish-white tabular crystals, melting at 96° ; it dissolves, although with difficulty, in sodium hydrate solution, and is reprecipitated by hydrochloric acid.

α -Thiobenzamidonaphthalene, $\text{C}^{10}\text{H}^7\text{NH}(\text{CS.C}_6\text{H}_5)$, prepared in a similar manner from the amidine, $\text{C}^{10}\text{H}^7\text{NH.C}(\text{NH})_2\text{C}_6\text{H}_5$, crystallises in yellow glistening plates melting at 147.5° .

The amidines here referred to are obtained as hydrochlorides on heating naphthylammonium chloride with acetonitril and benzonitril respectively (see Bernthsen a. Trompeter).

Bromo- α -amidonaphthalene.—The acetyl-derivative of this compound is formed on the addition of the calculated amount of bromine to α -acenaphthalid suspended in carbon bisulphide. *Bromo- α -acetamidonaphthalene*, $\text{C}^{10}\text{H}^7\text{Br.NHC}_2\text{H}_3\text{O}$, crystallises from hot alcohol, in which it is easily soluble, in long concentrically grouped needles melting at 193° . It is less readily decomposed than acenaphthalid by alkalis; by boiling it, however, with a solution of 3 pts. potassium hydrate and 2 pts. water, *bromo- α -amidonaphthalene* or *bromo- α -naphthylamine*, $\text{C}^{10}\text{H}^7\text{Br.NH}_2$, is produced. This compound crystallises from alcohol in aggregates of brown-coloured needles, melting at 94° , possessing an extremely unpleasant odour. It furnishes a very well crystallised hydrochloride and sulphate. As it may be converted into α -bromonaphthalene by displacement of the amido-group by hydrogen, it is an $\alpha\alpha$ -derivative of naphthalene (Rother, *Ber.* iv. 850).

Chloro- α -amidonaphthalene, $\text{C}^{10}\text{H}^7\text{Cl.NH}_2$.—Seidler has observed the formation of

this compound, together with naphthylamine, on reducing nitronaphthalene with tin and hydrochloric acid; it appears to result from the action of the stannic chloride which is produced on the naphthylamine, as it may be obtained by exposing a mixture of these substances to the air for several weeks. The body thus produced crystallises in colourless odourless needles melting at 98° ; it is sparingly soluble in benzene, and may therefore by means of this solvent be separated from naphthylamine, but easily soluble in alcohol and ether. Its *acetyl* derivative, $C^{10}H^8Cl.NHC^2H^3O$, crystallises in colourless needles melting at 184° , easily soluble in alcohol and ether (*ibid.* xi. 1201).

Nitro- α -amidonaphthalenes.—If a cold saturated solution of 3 pts. acenaphthalide in glacial acetic acid be mixed with 1 pt. of fuming nitric acid free from nitrous acid and the mixture allowed to stand several hours, a crystalline mass is deposited and a further quantity of crystals may be separated by mixing the supernatant liquid with water. The product is a mixture of two isomeric *nitro- α -acetamidonaphthalenes*, $C^{10}H^8(NO^2).NHC^2H^3O$, which, however, are nearly of the same solubility; on this account, they have not been separated in a state of purity (Andreoni a. Biedermann, *Ber.* vi. 342; Liebermann a. Dittler, *Liebig's Annalen*, clxxxiii. 228).

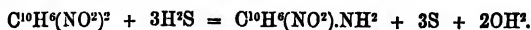
α -Nitro- α -amidonaphthalene, $C^{10}H^8(NO^2).NH^2$.—On heating the mixture of nitro-acenaphthalids thus prepared with an alcoholic solution of potassium hydrate (4 pts. nitro-product to 1–1½ pt. KOH), and keeping the liquid in gentle ebullition for about an hour, a mixture of the corresponding nitronaphthylamines is obtained, consisting chiefly, however, of that melting at 164° , which is less soluble than the isomeride in alcohol, and may therefore be purified by repeated recrystallisation from this solvent. It crystallises in thin orange-coloured needles, often matted together, moderately soluble in alcohol and glacial acetic acid; it possesses considerable tinctorial power for wool, which it colours orange-yellow. It is almost destitute of basic properties, for, although it dissolves more readily on warming in acids than in water, it separates out unchanged as the solution cools.

When submitted to the action of nitrous acid in alcoholic solution, it yields a compound of the formula $C^{10}H^{13}N^3O^4$, which is probably the nitro-derivative of so-called azodinaphthylidiamine (vii. 849; comp. Martius, *Jahresb.* 1865, 436).

The diazo-derivative formed by the action of nitrous acid in presence of nitric acid, however, is converted into α -nitronaphthalene on boiling with alcohol: hence both the amido- and nitro-groups occupy α -positions.

β -Nitro- α -amidonaphthalene, which is formed together with the foregoing, has not been obtained quite pure; it very closely resembles the α -compound, but is more soluble, and appears to melt at about 158° . It yields a complex azo-derivative when submitted to the action of nitrous acid in presence of nitric acid (Liebermann a. Dittler).

An *α -nitroamidonaphthalene* isomeric with the above is obtained on reduction of α -dinitronaphthalene (m. p. 212°). This latter compound, however, is very readily converted into the corresponding diamidonaphthalene, and special precautions are necessary in preparing the amidonitro-derivative from it. Alcohol having been poured over it, a couple of grams of a concentrated solution of ammonia are added, and the cooled liquid is then saturated with hydrogen sulphide; when this is the case, the vessel is set aside until the odour of the gas has disappeared, and then hydrogen sulphide is again passed into the liquid. These operations are repeated until the flask has gained in weight to the extent required by the equation:



The solution is then mixed with water, and the precipitate extracted with boiling dilute hydrochloric acid; the hydrochloric acid solution having been concentrated, ammonia is added; the precipitate is dissolved in a large quantity of dilute sulphuric acid; and the crystals of the sulphate which separate as the solution cools are recrystallised from water acidulated with sulphuric acid. The free base may be obtained by treating the sulphate with ammonia. It crystallises from boiling water in glistening small rod crystals, melting at 118° – 119° . The sulphate, $[C^{10}H^8(NO^2)(NH^2)]^2H^2SO^4.2H^2O$, forms long glistening needles, very difficultly soluble in cold water. α -Nitronaphthalene is obtained from this nitroamidonaphthalene on displacing the amido-group by hydrogen (Beilstein a. Kuhlberg, *Liebig's Annalen*, clxix. 87).

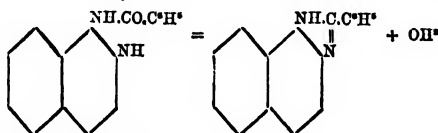
$\alpha\beta$ -Dinitro- α -amidonaphthalene, $C^{10}H^8(NO^2)^2.NH^2$.—The acetyl-derivative of this compound is formed on nitration of acenaphthalide. A concentrated solution of the latter in glacial acetic acid is mixed with a quantity of fuming nitric acid free from nitrous acid equal in weight to that of the acenaphthalide employed, and the mixture heated for a short time on the water bath to such a temperature that a slight evolution of gas takes place; the crystalline product which separates on standing is then washed and recrystallised from alcohol or glacial acetic acid. *Dinitro- α -acenaphthalid*

crystallises in long yellowish needles, melting at 247° . When boiled with a solution of sodium hydrate, it yields dinitro- α -naphthol, $C^{10}H^6(NO^2)_2.OH$ (m. p. 138°); but if heated with an alcoholic solution of ammonia for three hours at 140° , dinitro- α -amido-naphthalene is formed. The latter crystallises in lemon-yellow needles, melting at 235° (Liebermann a. Hammerschlag, *Liebig's Annalen*, clxxxiii. 272).

β -Nitro- α -bromo- α -amidonaphthalene.—To prepare this compound, α -bromo- α -acetamidonaphthalene, $C^{10}H^6Br.NH.CO^2H^3$, is nitrated, and 10 pts. of the resulting nitro-derivative, which crystallises in long pale-yellow needles melting at 232° , are boiled for two days with 2 pts. of potassium hydrate dissolved in 60 pts. anhydrous alcohol. It crystallises in long orange-coloured needles, melting at 200° ; on oxidation with nitric acid, it yields phthalic acid. It is abundantly soluble in concentrated sulphuric acid; after a time, colourless needles of the sulphate separate from the solution, but these are immediately decomposed by water (Liebermann a. Scheiding, *ibid.* clxxxiii. 258).

α -Benzamidonaphthalene, $C^{10}H^7.NH.CO^2H^3$, prepared by heating naphthylamine with benzoic chloride (Church), crystallises from alcohol, in which it is easily soluble, in glistening needles, melting at 156° (Ebell, *Ber.* vii. 1317; viii. 562). It yields two, if not three, isomeric mononitro-compounds on nitration. **α -Nitro- α -benzamidonaphthalene**, $C^{10}H^6(NO^2).NH.CO^2H^3$, crystallises from alcohol, in which it is difficultly soluble, in yellowish prisms melting at 224° . When boiled with potassic hydrate solution, it yields α -nitro- α -naphthol (m. p. 164°). On reduction with tin and hydrochloric acid, this compound is converted into the corresponding **amido-benzamidonaphthalene**, $C^{10}H^6(NH^2).NH.CO^2H^3$. The latter crystallises from alcohol in needles melting at 186° . Its hydrochloride forms fine colourless microscopic needles difficultly soluble in water and alcohol.

β -Nitro- α -benzamidonaphthalene, $C^{10}H^6(NO^2).NH.CO^2H^3$, crystallises in yellow glistening prisms, melting at 175° ; it is easily soluble in hot, but difficultly in cold water. It differs considerably from the isomeride in its behaviour on reduction with tin and hydrochloric acid, being converted into the hydrochloride of a base of the formula $C^{17}H^{12}N^2$ (so-called *anhydrobenzoyldiamidonaphthalene*). Probably the nitro-group's, in the first instance, reduced to the amido-group, the hydrogen-atoms of which then unite with the oxygen atom of the benzoyl group, forming water, thus:



β -Amido- α benzamidonaphthalene.

The base in question forms well-defined yellow crystals, melting at 210° , difficultly soluble in water, easily in alcohol. It appears to combine directly with amyl iodide. The hydrochloride, $C^{17}H^{12}N^2Cl$, crystallises in colourless microscopic needles, difficultly soluble in water and alcohol. The nitrate, $C^{17}H^{12}N^2NO_3$, crystallises in long yellow needles.

$\alpha\beta$ -Dinitro- α -benzamidonaphthalene, $C^{10}H^5(NO^2)_2.NH.CO^2H^3$, produced on nitrating α -benzamidonaphthalene with strong nitric acid, crystallises in small needles melting at 252° , difficultly soluble in alcohol, benzene, and chloroform. By recrystallisation from glacial acetic acid, it is converted into dinitroacetamidonaphthalene. On reduction with tin and hydrochloric acid, it is converted into **diamido- α -benzamidonaphthalene**, $C^{10}H^4(NH^2)_2.NH.CO^2H^3$ (Ebell).

Succinamidonaphthalene.—See Hanemann (*Ber.* x. 1713).

Diamidonaphthalenes.—The properties of the diamidonaphthalenes formed on reduction of so-called α - and β -dinitronaphthalene have been further investigated and described by De Aguiar (*Ber.* vii. 307).

According to Beilstein a. Kuhlberg (*Liebig's Annalen*, clxix. 90), there is a great difference in the behaviour of α - and β -dinitronaphthalene with reducing agents, the latter being only slowly acted upon even by tin and hydrochloric acid (comp. Ladenburg, *Ber.* xi. 1651).

A third **diamidonaphthalene**, isomeric with those from the two dinitronaphthalenes, has been obtained from α -nitro- α -acetamidonaphthalene by Liebermann a. Dittler (*Liebig's Annalen*, clxxxiii. 238). To prepare it, the latter compound is treated with tin and hydrochloric acid, the dissolved tin is removed by means of hydrogen sulphide, &c., and the resulting **α -amido- α -acetamidonaphthalene hydrochloride** is boiled with a dilute solution of sodium hydrate; the base then separates as a resin. From this product, salts may be obtained by dissolving it in dilute acid and then precipitating

the filtered solution with the concentrated acid. The *chloride*, $C^{10}H^8(NH^2Cl)^2$, forms small white plates; on mixing its solution with a dilute solution of potassium dichromate or chromic acid, a green coloration is produced; more concentrated solutions furnish a similarly coloured precipitate. On boiling, the colour disappears, and naphthaquinone distils over. When the diamidonaphthalenes from α - and β -dinitronaphthalene are thus treated, not a trace of quinone is produced.

α -Diamidonaphthalene may be obtained by precipitating a moderately concentrated solution of the iodide with sodium hydrate; a white precipitate is produced, which may be purified by recrystallisation from alcohol or ether. It crystallises from alcohol, chloroform, and ether in glistening needles or prisms, which, as a rule, are colourless, and sublimes almost without decomposition in white feather-like forms. It melts at 189.5° . It is somewhat soluble in cold, and readily soluble in hot water, and still more in alcohol, ether, and chloroform. The dry substance does not alter, even on exposure to light. On the addition of ferric chloride to water in which crystals of the base are suspended, a blue-violet coloration is produced, and after a time a similarly coloured precipitate forms. A like coloration results on adding barium dioxide and hydrochloric acid, or potassium nitrite and sulphuric acid, to an alcoholic solution; potassium hypochlorite causes a red coloration and precipitate.

β -Diamidonaphthalene may be prepared in a similar manner, but a more concentrated solution of the iodide should be employed, and it is more difficult to purify: the precipitate is dissolved in cold strong alcohol, and the solution mixed with double the amount of distilled water; the base then separates out in white needles melting at 66.5° . It is more soluble than the α -compound in water, but less soluble in chloroform; it dissolves in alcohol and ether in all proportions, but cannot be obtained well crystallised from either of these solvents. No characteristic coloration is produced on the addition of barium dioxide and hydrochloric acid to the alcoholic solution, the liquid being at most slightly blackened; ferric chloride produces a dark chestnut-brown precipitate.

Both α - and β -diamidonaphthalene combine readily with oxalic acid. The α -oxalate crystallises from water in thin transparent plates; the β -oxalate in white glistening crystals like those of potassium iodide. The latter appears readily to undergo change, and is said by De Aguiar to furnish a substance resembling gold in appearance and lustre and of great stability, but the nature of this substance and the method of preparing it have not been described (comp. *Ber.* vii. 313).

The α -diamine is not appreciably acted upon by ethyl oxalate at 100° , but if the β -diamine be heated with 10 pts. of the oxalate in sealed tubes at 100° , a compound of the formula $C^{14}H^{12}O^2$ is produced, which crystallises from chloroform in magnificent red needles like chromic anhydride; this compound is soluble in water, alcohol, and benzene; it carbonises without melting if heated to 195° . It is regarded by De Aguiar

as *ethylnaphthaleneoxamide*, $C^{10}H^8(C^2H^3) \begin{matrix} \text{NH.CO} \\ | \\ \text{NH.CO} \end{matrix}$; the formula $C^{10}H^8 \begin{matrix} \text{NH.CO} \\ | \\ \text{N}=\text{C.OC}^2\text{H}^3 \end{matrix}$ would, however, appear more probable.

The α -diamidonaphthalene or one of its salts be submitted to the action of nitrous acid or potassium nitrite, a brownish-black flocculent product is obtained. But if a solution of the sulphate of the β -diamine be mixed with a concentrated solution of a single molecular proportion of potassium nitrite, a voluminous red precipitate is produced, which may be recrystallised from warm benzene, in which it is easily soluble. It then forms extremely fine glistening red needles. This product has the composition $C^{10}H^7N^3$; its properties are altogether different, however, from those of the ordinary diazo-derivatives. It is a very stable compound in the free state, and may even be partially sublimed; the sublimed substance resembles alizarin in appearance. It forms compounds both with acids and with bases, but they are highly unstable, and at once decomposed by water. Thus if the moist substance be added to a mixture of equal volumes of water and sulphuric acid, a dark wine-red coloured solution is obtained which soon deposits long needle-like crystals of the same colour; the least trace of water, however, turns these crystals vermilion-red, the parent substance being regenerated.

According to Ladenburg (*Ber.* xi. 1650), the β -diamine alone reacts in the manner characteristic of orthodiamido-compounds with benzoic aldehyde.

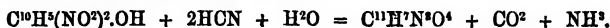
Naphthydrene-glycol, $C^{10}H^{10}(OH)^2$ (Grimaux, *Compt. rend.* lxxv. 351, lxxvi. 575; *Bull. Soc. Chim.* [2], xviii. 205; xix. 396). The dichlorinated derivative of this alcohol is produced by prolonged boiling of naphthalene tetrachloride with water; it crystallises from the concentrated solution in brownish granules or crystalline plates, but may be rendered colourless by means of animal charcoal. It dissolves in about 30 pts. of boiling water, but is sparingly soluble in cold water; alcohol and ether

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dissolve it readily. It separates from an ethereal solution in hard prisms of considerable size, melting at 155° – 166° . The *diacetyl* derivative, $C^{10}H^6Cl^2(OC^2H^3O)^2$, crystallises from ether in plates or short prisms melting at 130° – 131° ; the corresponding *dibenzoate*, $C^{10}H^6Cl^2(OC^2H^3O)^2$, melts at 148° – 150° .

On distillation with hydrochloric acid, dichloronaphthylene glycol furnishes a small amount of a monochloronaphthol, $C^{10}H^6Cl.OH$, crystallising in long fine needles melting at 109° . If an aqueous solution be distilled with zinc-dust, α -naphthol is produced in accordance with the equation $C^{10}H^6Cl^2(OH)^2 + 2H = C^{10}H^7.OH + 2HCl + H^2O$. If heated with 30 pts. of water at 150° for twenty-four hours, it yields a resinous product, together with a crystalline substance, which is apparently α -naphthaquinol. On oxidation with dilute nitric acid, it is converted into phthalic acid.

Naphthylpurpuric Acid, $C^{11}H^7N^3O^4$. The salts of this acid are formed in precisely the same manner as the corresponding isopurpurates (iii. 433) from the potassium salt obtained by the action of potassium cyanide on dinitronaphthol in alcoholic solution (Sommaruga, *Ber.* iv. 94):



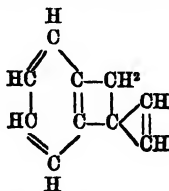
They are dark golden-brown with metallic reflex; the potassium salt is crystalline; the 'acid' itself cannot be isolated. On oxidation with nitric acid, they yield a mixture of mono- and dinitronaphthol; when heated with potassic hydrate they form hemimellithic, phthalic, and benzoic acid.

If, in preparing potassium naphthylpurpurate, aqueous solutions be employed instead of alcoholic, a second body, so-called *indophan*, $C^{22}H^{10}N^4O^4$, is also obtained. To prepare this compound, about 30 grams of dinitronaphthol are added to about 2 litres of water, and sufficient ammonia mixed with the boiling liquid to dissolve the dinitronaphthol. A hot concentrated solution of 45 grams pure potassium cyanide is then added. The reaction is complete within about ten minutes. The whole is then placed on a good filter, and the solid residuo washed with boiling water until the liquid runs through colourless. The product is a mixture of indophan with its potassium derivative. After further prolonged washing with boiling water, it is removed from the filter and heated with very dilute hydrochloric acid, again filtered and washed until the filtrate no longer contains chlorine. If it be desired to prepare the potassium derivative, the crude product is heated with potassic hydrate solution, filtered, and then washed until freed from alkali.

Indophan is a violet-coloured powder with a green metallic lustre. It is insoluble in the ordinary solvents, but moderately soluble in sulphuric or warm glacial acetic acid; it does not crystallise from these solutions, however; and, unlike indigo, cannot be sublimed. It is oxidised by nitric acid, but cannot be reduced by ferrous sulphate and lime. It yields the same products as naphthylpurpuric acid on fusion with potassic hydrate. The potassium and sodium derivatives, which closely resemble indigo in outward appearance, contain only a single atom of metal.

CONSTITUTION OF NAPHTHALENE AND ITS DERIVATIVES.

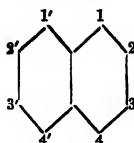
The adaptability of the formula originally proposed for naphthalene by Erlenmeyer in 1866 (*Liebig's Annalen*, cxxxvii. 346), but first established on the basis of experimental evidence by Graebe in 1869 (vi. 212), has been entirely confirmed by all recent researches (comp. Ladenburg, *Ber.* vii. 1137). Wrelen, however, has proposed (*ibid.* ix. 590) the following as a substitute for the Erlenmeyer-Graebe formula:



but there does not appear to be the slightest experimental evidence to justify the use of this symbol.

In discussing the constitution of the naphthalene derivatives, it is convenient, as in the case of the benzene derivatives, to disregard the mode of union of the carbon atoms, and merely to employ a double hexagon as the symbol of naphthalene, numbering the 'positions' in the one hexagon 1, 2, 3, and 4, and the *corresponding* 'positions' in the other hexagon 1', 2', 3', and 4', thus:

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The data as yet accumulated are not sufficient to furnish a complete solution of the problem of the constitution of the naphthalene derivatives, but they are sufficient for the preliminary discussion of the problem and well worthy of consideration in detail.

On reference to the naphthalene symbol, it will be obvious that two, but only two, mono-derivatives are possible, viz.: one formed by the displacement of the hydrogen atoms in the positions 1, 4, 1' or 4', the other formed by the displacement of those in the positions 2, 3, 2' or 3'. Also that two, but only two, 'symmetrical' di-derivatives are possible, in which the positions 1 : 4' (= 1' : 4) or 2 : 3' (= 2' : 3) are occupied; in like manner, there may be two symmetrical tetra-derivatives.

The two isomeric (α and β) naphthalenesulphonic acids, formed simultaneously by the action of sulphuric acid on naphthalene, are respectively representative of these two kinds of mono-derivatives.

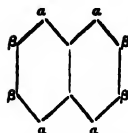
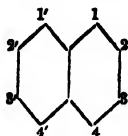
Ordinary nitronaphthalene and the amidonaphthalene (naphthylamine) derived from it, α -naphthol, α -cyanonaphthalene, the bromonaphthalene formed by the direct action of bromine on naphthalene and α -naphthoic or naphthalene- α -carboxylic acid are all to be regarded as members of the same series of mono-derivatives as the so-called naphthalene- α -sulphonic acid: since α -naphthol is obtained by directly displacing the sulpho-group in this acid by the group OH; since α -naphthol may be formed by Griess's method from amidonaphthalene (naphthylamine); and since naphthalene- α -carboxylic acid may be obtained on the one hand from the cyanonaphthalene derived from the α -sulphonic acid, and on the other from ordinary bromonaphthalene by the combined action of sodium and ethyl chloroformate, $\text{Cl.COO}^{\text{C}}\text{H}^{\text{B}}$ (Eghis). Ordinary chloronaphthalene is doubtless also an α -derivative, as it corresponds in all particulars to ordinary bromonaphthalene.

Naphthalene- β -sulphonic acid is the only β -derivative as yet obtained by a direct process from naphthalene. To it correspond β -naphthol, β -cyanonaphthalene, naphthalene- β -carboxylic acid, β -naphthylamine, and the chloro- and bromonaphthalene formed from this latter by Griess's method.

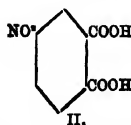
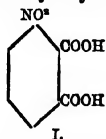
The positions 1, 4, 1' and 4' in the naphthalene symbol are to be regarded as α -positions, i.e. it is by the displacement of a hydrogen atom in one of these positions that the α -mono-derivatives are formed, and the positions 2, 3, 2' and 3' are to be regarded as β -positions. The evidence on which these two propositions are based is briefly as follows:

Supposing any di-derivative of naphthalene in which both the radicles substituted for hydrogen are in the same hexagon, and in which both radicles are either in α -positions or in β -positions, be taken and the relative positions of these two radicles be determined, then, if the two radicles be found to occupy the relative positions 1 : 2, it follows that the hydrogen atom in the positions marked 2 and 3 in the above symbol have been displaced; while if they occupy the relative positions 1 : 4, those marked 1 and 4 in the symbol have been displaced. Now Liebermann and Dittler have shown (*Liebig's Annalen*, clxxxiii. 228) that by nitrating acetamidonaphthalene (acenaphthalid), $\text{C}^{10}\text{H}^{\text{A}}.\text{NH}(\text{C}^{\text{A}}\text{H}^{\text{O}})$, prepared from ordinary or α -amidonaphthalene, then converting the acetamidonitronaphthalene, which is the chief product of the reaction (comp. p. 1371), into amidonitronaphthalene, and displacing the amido-group in this latter by hydrogen by Griess's method, a nitronaphthalene is obtained in all respects identical with ordinary or α -nitronaphthalene; in other words, both radicles in the acetamidonitronaphthalene in question occupy α -positions. By reducing the same acetamidonitronaphthalene, then converting the resulting acetamidoamidonaphthalene into diamidonaphthalene, $\text{C}^{10}\text{H}^{\text{A}}(\text{NH}^{\text{A}})^2$, and oxidising this latter, naphthaquinone, $\text{C}^{10}\text{H}^{\text{A}}(\text{O}^{\text{A}})^2$, is produced: hence each of the oxygen-atoms in naphthaquinone is in the α -position, and as naphthaquinone yields phthalic acid on oxidation, the substituting radicles in the various derivatives referred to are in the one hexagon. There can be little doubt, from the complete similarity of their properties, that naphthaquinone and benzoquinone are similarly constituted: and since it has been shown that the oxygen-atoms in the latter occupy relatively the positions 1 : 4, it is in the highest degree probable that naphthaquinone is also a 1 : 4 derivative. If this deduction be accepted, it necessarily follows that the positions 1, 4 and also those marked 1' 4' in the naphthalene symbol are α -positions; and therefore that the positions 2, 3 and 2' 3' are β -positions, thus:

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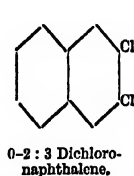
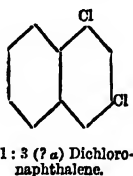
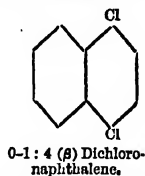
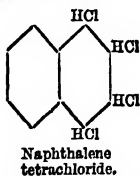


But, as Reverdin & Nölting have pointed out (*Ber.* xiii. 36), the force of this argument is somewhat diminished by the fact that two naphthaquinones are known. The following argument which these chemists have brought forward is, however, perfectly conclusive. Obviously only two isomeric nitrophthalic acids are possible, viz.:

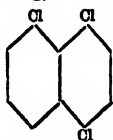


Two such acids have actually been prepared, both being formed on nitration of phthalic acid (Miller, *Ber.* xi. 1191); they melt respectively at 212° and 165° . Now, Miller has shown that the modification which melts at 165° is convertible into a hydroxyphthalic acid which Schall has proved to have the constitution $\text{OH} : \text{COOH} : \text{COOH} = 1 : 3 : 4$; hence it follows that the nitrophthalic acid melting at 212° is represented by fig. I., and that melting at 165° by fig. II., and since the former may be obtained by oxidation of nitronaphthalene (Beilstein & Kurbatow, *Ber.* xii. 688), which is an α -derivative, it follows that the α -position in the symbol of naphthalene is the position next the carbon atom common to the two hexagons.

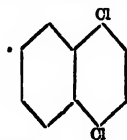
Constitution of the Haloid-derivatives of Naphthalene. Chloronaphthalenes.—The dichloronaphthalene melting at 68° (so-called β), obtained from naphthalene tetrachloride, undoubtedly contains both chlorine atoms in the same C^{α} -group in the relative positions 1 : 4, since it may be obtained from α -nitro- α -naphthol and yields a dichlorophthalic acid on oxidation. The isomeric dichloronaphthalene (m. p. 35° , so-called α) obtained from the same tetrachloride, is perhaps the 0-1 : 3 modification, for, from the general behaviour of naphthalene, it might be expected that this modification, rather than the isomeric 0-2 : 3 dichloronaphthalene, would be formed by the removal of the elements of two molecules of hydrogen chloride from the tetrachloride, which it is obvious may furnish three dichloronaphthalenes. If, however, the dibromonaphthalene obtained by Meldola is isomeric with that of Jolin, it is more probable that it is the 0-2 : 3 modification:



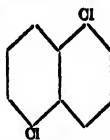
The dichloronaphthalene melting at 107° (so-called γ) is shown, by its behaviour on oxidation, to contain the chlorine atoms in different C^{α} -groups; both chlorine-atoms, however, are in α -positions, since it may be obtained both from nitronaphthalene- α -sulphonic acid and from α -nitronaphthalenesulphonic acid. Both β - and γ -dichloronaphthalene, however, may be converted into so-called δ -trichloronaphthalene by distilling their mono-nitro-derivatives with PCl_5 ; and hence it follows that the three chlorine-atoms in δ -trichloronaphthalene are all in α -positions. But δ -trichloronaphthalene is also obtained on treatment of β -dinitronaphthalene with PCl_5 , so that indirectly it may be said to be formed by further chlorination of ζ -dichloronaphthalene (m. p. 83°), as this latter is produced on simply displacing the nitro-groups in β -dinitronaphthalene by chlorine; hence ζ -dichloronaphthalene is also an $\alpha\alpha$ -derivative (Atterberg). But if β -dichloronaphthalene be the 0-1 : 4 modification, γ -dichloro-



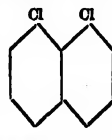
δ -Trichloronaphthalene.



β -Dichloronaphthalene.



γ - and ζ -Dichloronaphthalene.



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naphthalene must be the 1-4', and ζ -dichloronaphthalene the 1-1' modification, or *vice versa*.

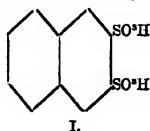
It is most probable that the γ -modification is the 1-4' compound, as it is derived from the dinitronaphthalene which is the chief product of the action of nitric acid on naphthalene, it being apparently the tendency in the naphthalene series for the more symmetrically constituted compound (*i.e.* the more symmetrical as far as the symbol is concerned) to be formed in preference. The difference in the behaviour of the diamidonaphthalenes obtained from α - and β -dinitronaphthalene also tends to support this conclusion.

The above conclusions derive further support from the following considerations. By submitting nitro- γ -dichloronaphthalene to reduction, an amidochloronaphthalene is obtained which necessarily corresponds either to β - or ζ -dichloronaphthalene, since the nitro-derivative in question is convertible into δ -trichloronaphthalene. It is isomeric, however, with the amidochloronaphthalene (m. p. 85°) which corresponds to the former, and therefore corresponds to the latter, which may, in fact, actually be obtained from it by Griess's method (Atterberg).

The existence of three dichloronaphthalenes having their chlorine-atoms all in α -positions is also a proof of the existence of four α -positions in naphthalene. Chlorine and the nitro-group respectively occupy the same position in chloronaphthalene and nitronaphthalene, since the latter may be directly converted into the former by displacement of the NO_2 -group by Cl. But, on the one hand, chloronaphthalene yields a nitro-derivative which is directly convertible into β -dichloronaphthalene. Nitronaphthalene, on the other hand, is convertible into two isomeric dinitronaphthalenes, corresponding respectively to γ - and ζ -dichloronaphthalene. Hence β -, γ - and ζ -dichloronaphthalene each contain an atom of chlorine in the same position as the NO_2 group in nitronaphthalene; but the second chlorine-atom must occupy a different position in each relatively to the first, otherwise they would not be isomeric: consequently there must be at least four α -positions in naphthalene (Atterberg).

The constitution of the remaining dichloronaphthalenes cannot at present be conjectured with any great degree of certainty. The η -modification (m. p. 48°) is not improbably a 2-1' or 2-4' derivative, as it is derived from naphthalene- β -sulphonic acid, and it is probable from the behaviour of the α -sulphonic acid on nitration that the nitro-group in the nitro- β -sulphonic acid occupies an α -position in the C⁶-group which is not occupied by the sulphy-group.

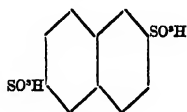
δ - and ϵ -dichloronaphthalenes, which are derived from the isomeric naphthalene-disulphonic acids, are probably, one or both, $\beta\beta$ -derivatives. Both probably are derived from the β -monosulphonic acid; but supposing this to be the case, and that the β -disulphonic acid contains both sulphy-groups in β -positions, there are still three formulæ which may be applied to it, *viz.*:



I.



II.

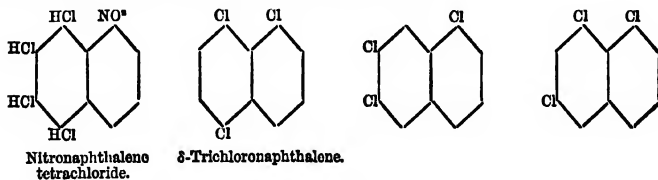


III.

According to Ebert a. Merz, the naphtholsulphonic acid formed on fusing the β -disulphonate with potassium hydrate is identical with that produced from β -naphthol and sulphuric acid; if this be the case, the first of the above formulæ would appear to be the most probable, for as the action of sulphuric acid and bromine on the phenols is similar in so far as the constitution of the resulting compounds is concerned, as β -naphthol yields a bromo-derivative in which both bromine and the OH-group are in the same C⁶-group (Smith), it is probable that the sulphy-acid derived from β -naphthol would contain both the OH- and the sulphy-group in the same C⁶-group. If, however, the β -disulpho acid were thus constituted, the dicarboxylic acid derived from it should be identical with naphthopthalic acid, $\text{C}^{10}\text{H}^6(\text{COOH})_2$, which is not the case. It is therefore a question whether the naphtholsulphonic acid from the β -disulphonic acid and that from β -naphthol are identical, as Ebert a. Merz have stated, or whether isomeric change does not take place in some of the reactions above referred to. The fact that it is the C⁶-group which does not contain the sulphy-group that is attacked when naphthalene- α - and β -sulphonic chlorides are submitted to the action of chlorine, or when naphthalene- α -sulphonic acid is treated with nitric acid, renders it probable that the naphthalenedisulphonic acids also contain the sulphy-groups in distinct hexagons, and such a conclusion would appear to harmonise well with their general behaviour and that of the compounds derived from them. On this assumption, the second and third of the formulæ given above are the most probable expressions of the constitution of the α - and β -disulphonic acids respectively.

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α -Trichloronaphthalene is perhaps the 0-1:2:4 modification, as it yields a nitrotrichlorophthalic acid on oxidation with nitric acid (Widmann). δ -Trichloronaphthalene, as already pointed out, is a 1:4-1' derivative. β - and γ -Trichloronaphthalene are probably both derived from the same nitronaphthalene tetrachloride, and, supposing this to be the case, there are only two formulæ which can be assigned to them, since the third modification which can be formed from such a tetrachloride is a body of the formula of δ -trichloronaphthalene, thus:



The β -compound is not improbably the 1-1':3, and the γ -compound the 1-2':3' modification. ζ -Trichloronaphthalene being formed by a reaction similar to that by which the γ -compound is produced, excepting that the β - instead of the α -sulphonic chloride is employed, may be regarded as the 2-2':3' modification.

From the manner in which they are formed, and from their behaviour with nitric acid, it may be suggested as more or less probable that the remaining chloronaphthalenes are bodies of the following constitution:

α -Tetrachloronaphthalene, m. p.	1:4 - 2':3'
β " "	1 - 2':3':4'
γ " "	1:4 - 1':3'
δ " "	1 - 1':2':4'
ϵ " "	1:4 - 1':4'
α -Pentachloronaphthalene, "	1 - 1':2':3':4'
β " "	1:4 - 1':2':4'

Bromonaphthalenes.—It is to be supposed that these correspond in constitution with the chloronaphthalenes prepared by similar methods. According to Guareschi, however (*Gazz. chim. ital.* vii. 24), the dibromonaphthalene melting at 81° (that termed β -dibromonaphthalene by Jolin) yields a bromophthalic acid on oxidation with nitric acid, and Meldola finds that the same acid is obtained by reducing the mononitro-derivative of the dibromonaphthalene in question and oxidising the product (*Ber.* xii. 1963). This result, as the latter points out, appears to indicate that the bromine-atoms in β -dibromonaphthalene are not both in the same C⁶-group. Its production from nitro- α -bromonaphthalene and from α -bromonaphthalenesulphonic acid, and the fact that the latter acid is converted into β -dichloronaphthalene when distilled with PCl₅ (Jolin), seem, however, to negative this assumption.

Nitronaphthalenes and Nitrochloronaphthalenes.—The conversion of the two dinitronaphthalenes produced by nitration of naphthalene into γ - and ζ -dichloronaphthalene would appear to indicate that the so-called α -compound is the 1-4', and the β -compound the 1-1' modification. The third isomeride obtained by Liebermann a. Hammerschlag is undoubtedly the 0-1:3 modification.

The constitution of the nitrochloronaphthalenes may be inferred from that of the chloronaphthalenes into which they are converted on distillation with PCl₅, of course only in so far as these latter are bodies of known constitution.

Constitution of the α -Naphthol and α -Naphthylamine derivatives.—The researches of Liebermann and his pupils more especially leave no doubt that these compounds behave as the corresponding mono-derivatives of benzene, phenol and aniline. Thus both furnish two isomeric mono-derivatives, that produced in largest amount being formed by the displacement of an atom of hydrogen in the para-position relatively to the OH or NH₂ group (or rather to the NH.C²H³O group, since in most cases α -naphthalid and not naphthylamine is employed); and although it has not yet been directly proved, it can scarcely be doubted, that the isomeride which is formed at the same time contains the displacing radicle in the ortho-position relatively to the OH or NH₂ group. Both of these mono-derivatives furnish the same di-derivative when further acted upon, but the remaining hydrogen-atom, occupying the meta-position, resists displacement, and under what may be termed ordinary conditions di-derivatives only are obtained.

At present nothing is known of the laws which govern substitution in the case of the β -mono-derivatives of naphthalene.

H. E. A.

NAPHTHYLAMINES. See NAPHTHALENES, AMIDO- (p. 1369).

NAPHTHYL-KETONES. See KETONES (p. 1156).

NARCEINE, $C^{23}H^{23}NO^3$. This base dissolves sparingly in water, very easily in potash and in ammonia, and crystallises from aqueous solution with 2 mol. water, which are easily given off at 100° . At 140° another molecule of water is evolved, and the fused residue dissolves with moderate facility in dilute hydrochloric acid, forming a solution from which ammonia throws down amorphous flocks. The reaction, which takes place according to the equation $C^{23}H^{23}NO^3 = H^2O + C^{22}H^{22}NO^3$, yields probably four, and certainly three, products, of which all but one (*i.e.* three or two respectively) are amorphous and basic; the remaining substance, especially in alcoholic solution, gives a splendid blue colour with ferric chloride, but does not consist of gallic acid (O. Hesse, *Deut. Chem. Ges. Ber.* vii. 105).

Narceine, treated with zinc and hydrochloric acid, is converted into a base, $C^{22}H^{22}NO^3$, or $C^{22}H^{22}NO^3$, which is amorphous, and forms amorphous salts (Beckett & Wright, *Chem. Soc. J.* xxviii. 629).

Acetic anhydride appears to exert a dehydrating action on narceine. In two experiments, in which a distinct odour of nitrous acid was perceived and red fumes were given off, two bases soluble in ether were produced, one crystallised, $C^{23}H^{23}NO^3$, the other amorphous, $C^{22}H^{22}NO^3$ (Beckett & Wright).

When narceine is heated to 140° – 150° for fifteen to twenty hours with water in a sealed tube, it chars and becomes decomposed, but does not form either meconin, opianic acid, or hemipinic acid, or any solid base soluble in ether; a trace of methylamine is however produced.

Narceine, oxidised by potassium dichromate and sulphuric acid, gives off carbon dioxide, and yields about 10 p. c. of hemipinic acid and methylamine; with ferric chloride, considerable quantities of hemipinic but no opianic acid. Hemipinic acid is also produced, though in smaller quantity, by the action of sulphuric acid and manganese dioxide, or of potassium permanganate, on the aqueous solution of narceine.

Dilute solutions of potassium hydroxide and potassium carbonate act on narceine in such a manner as to form ammonia and trimethylamine, but no pyridine &c. allied volatile bases; also small quantities of an acid which is easily soluble in ether and in hot alcohol, sparingly soluble in water, and forms small white crystals melting at 210° . This acid has approximately the composition $C^{23}H^{23}NO^3$, and its formation from narceine may be represented by the equation $C^{23}H^{23}NO^3 - H^2O - 2H^2 = C^{23}H^{23}NO^3$. By fusion with potash, it yields an acid exhibiting all the reactions of protocatechuic acid, which latter is also formed, and in considerable quantity, when narceine is heated to 230° – 240° with potassium hydroxide, methylnormeconin being formed as an intermediate product.

These results lead to the representation of narceine by the formula:



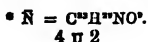
differing from that of oxynarcotine (p. 1383) only in the character of its nitrogenous radicle.

Hydrochlorides (A. Petit, *Bull. Soc. Chim.* [2], xviii. 534).—Narceine hydrochloride, as met with in commerce, contains a variable quantity of hydrochloric acid associated with the base. When narceine is dissolved in excess of acid, and the whole evaporated to dryness, the hydrochloric acid retained is smaller in quantity the longer the evaporation has been continued; if the base is dissolved in just sufficient acid, the solution does not deposit crystals if more water than 50 parts to 1 of narceine be present; with 25 to 1, crystals are deposited, the formula of which is $2(N.HCl).5H^2O$; * if 1 part of narceine be dissolved in 70 parts of dilute acid containing 3 grams to the litre mixed with 30 of water, crystals form on cooling, which have the composition $5N.HCl$; whilst if 30 of this acid and 70 of water be employed, the crystals are $10N.HCl$. This latter product is also obtained by the action of water on either of the hydrochlorides, $2(N.HCl).5H^2O$, or $5N.HCl$.

Narceine dissolves in 769 parts of water

$\bar{N} + HCl$	"	277	"
$\bar{N} + 2HCl$	"	150	"
$\bar{N} + 3HCl$	"	130	"
$\bar{N} + 4HCl$	"	50	"

Wright (*Chem. Soc. J.* xxvii. 109) finds that narceine hydrochloride, obtained from a solution containing 8 to 10 mols. hydrochloric acid to 1 mol. narceine, which



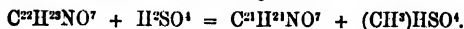
gives off water of crystallisation when heated to 100° , but recovers it over sulphuric acid—contains altogether a proportion of water larger than that assigned to it by Pettit ($2\frac{1}{2}\text{H}_2\text{O} = 8.26$ p. c., and $3\text{H}_2\text{O} = 9.75$ p. c.) By cooling a solution of N.HCl in 50 pts. water, a crystalline salt, 6N.HCl , was obtained, which, when treated with cold water, finally retained 0.76 p. c. chlorine, answering to Pettit's compound 10N.HCl , this quantity, however, being reduced by further digestion to 0.4 p. c. The last portion of chlorine could not be removed, even by precipitation with alkali and repeated crystallisation. When, however, narceine hydrochloride was boiled with strong hydrochloric acid, no compound was formed analogous to chlorocodide (vi. 480), but—according to the equation $\text{C}^{22}\text{H}^{29}\text{NO}^9.\text{HCl} = \text{H}_2\text{O} + \text{C}^{22}\text{H}^{27}\text{NO}^9.\text{HCl}$,—the hydrochloride of a new base, which is amorphous, slightly soluble in ether, easily in alkalis and alkaline carbonates. Its salts give with ferric chloride a dark blue-violet colour, afterwards turning brownish, and with potassium chromate and sulphuric acid, a reddish-violet colour.

Sulphates (Beckett a. Wright, *loc. cit.*)—The small quantity of chlorine which adheres so obstinately to narceine precipitated from the hydrochloride, is completely removed by solution in hot dilute sulphuric acid (8–10 p. c.) and repeated crystallisation of the resulting sulphate. The crystals thus purified, then drenched with fifty times their volume of water, and washed with alcohol and ether, have the composition $7\text{C}^{22}\text{H}^{29}\text{NO}^9.4\text{SO}^4\text{H}^2 + 10\text{H}_2\text{O}$. This salt crystallised from a warm mixture of sulphuric acid and water in equal volumes, yields crystals having the composition of a bibasic sulphate; and by repeatedly crystallising the first-described salt from a large quantity of water, products more and more basic are obtained containing 3, 4, and 5 mols. narceine to 1 mol. SO^4H^2 . The narceine sulphates are distinguished from the hydrochlorides—which they otherwise closely resemble—by the fact that they are completely decomposed by solution of sodium carbonate, and yield the free base perfectly pure.

Narceine Ethiodide, $\text{C}^{22}\text{H}^{29}\text{NO}^9.\text{C}^2\text{H}^3\text{I}$, prepared like the corresponding morphine and narcotine-compounds, may be obtained by evaporating the product to dryness and dissolving the amorphous residue in absolute alcohol, in granular crystals, which, when dried at 100° , have the composition $\text{C}^{22}\text{H}^{29}\text{NO}^9.\text{C}^2\text{H}^3\text{I}$. The mother-liquor, though no longer crystallisable, has the same composition. By exposure to air and light, the compound is ultimately converted into a blue substance resembling iodide of starch. From solution in ten times its volume of boiling alcohol of 90 p. c., the ethiodide separates on cooling quite unaltered, and in combination with 2 mols. water of crystallisation. Treated in alcoholic solution with moist silver oxide, it yields an alkaline liquid having the composition $\text{C}^{22}\text{H}^{29}\text{NO}^9.\text{C}^2\text{H}^3\text{OH}$, which however decomposes partially, even on spontaneous evaporation, into narceine and alcohol. A platinum salt prepared from it showed an amount of platinum approaching very nearly to that of the platinum-chloride of narceine.

On the whole, therefore, it seems that while narceine ethiodide is more stable than the salts of narceine with inorganic acids, the addition-derivatives of narceine, as a class, seem to be marked by a tendency to break up into narceine and the additive-substance employed. An analogous behaviour is also characteristic of narcotine; indeed it is probable that there is some constitutional similarity between these two bases, as each of them may be made to yield derivatives of protocathechuic acid (Beckett a. Wright, *Chem. Soc. J.* xxviii. 703).

NARCOTINE, $\text{C}^{22}\text{H}^{23}\text{NO}^7$. Narcotine heated on the water-bath with excess of dilute sulphuric acid (equal volumes of H_2O and H^2SO^4) is converted into dimethylnornarcotine (vi. 863), according to the equation



The methylsulphuric acid formed at the same time is further resolved into sulphuric acid and methyl alcohol. The reaction takes place exactly in the manner above represented, if the heating be interrupted as soon as the mass becomes flesh-coloured. By further heating, a second, and perhaps also a third atom of methyl may be removed from the narcotine, but the product is always impure (Armstrong, *Chem. Soc. J.* xxiv. 56).

On the action of *hydrogen sulphide* on narcotine in alcoholic solution, see ALKALOIDS (p. 56).

Hydrochloride of Narcotine, like the corresponding narceine salt (p. 1379), becomes more basic the oftener it is recrystallised from hot water, the salts $5\text{C}^{22}\text{H}^{23}\text{NO}^7.\text{HCl}$, $7\text{C}^{22}\text{H}^{23}\text{NO}^7.\text{HCl}$, and $8\text{C}^{22}\text{H}^{23}\text{NO}^7.\text{HCl}$, being formed in succession (Beckett a. Wright, *Chem. Soc. J.* xxix. 164).

Oxidation-products of Narcotine.

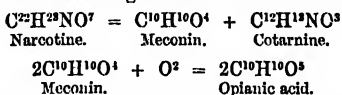
Cotarnine, $C^{12}H^{13}NO^3$, and **Hydrocotarnine**, $C^{12}H^{13}NO^3$ (Beckett a. Wright, *Chem. Soc. J.* 1875, 573-585; 1876, i. 164-174, 281-309, and 461-474). Cotarnine prepared by oxidising narcotine with sulphuric acid and manganese dioxide, melted at 126° , and when crystallised from benzene was found to have exactly the composition $C^{12}H^{13}NO^3 \cdot H^2O$, the molecule of water not being separable without simultaneous decomposition of the base. The *platinochloride*, $(C^{12}H^{13}NO^3 \cdot HCl)^2PtCl^4$, may however be obtained anhydrous by prolonged desiccation over sulphuric acid.

Hydrocotarnine, first obtained by Hesse from the mother-liquors of the preparation of morphine by the Robertson-Gregory process (vii. 876), is also formed by the action of granulated zinc on cotarnine dissolved in dilute hydrochloric acid, the reaction being continued for several days, and the liquid all the time being kept slightly acid. The hydrocotarnine may then be separated by addition of excess of ammonia, and agitation with ether, from which it crystallises in prisms often an inch long. It dissolves easily also in alcohol and in benzene; melts at 55° when pure, at lower temperatures when impure (50° according to Hesse); gives off water of crystallisation at 60° , and then does not solidify till after some time. The base prepared as above gave with sulphuric acid the dirty red-violet coloration described by Hesse. Its solution in hydrochloric acid yielded on evaporation over sulphuric acid crystals having the composition $C^{12}H^{13}NO^3 \cdot HCl + H^2O$. Hesse found $1\frac{1}{2}H^2O$, probably because the last portions of water are somewhat obstinately retained, and can be driven off only by reducing the salt to fine powder and leaving it to stand for some time.

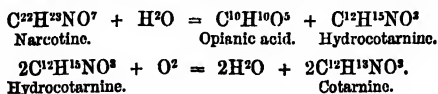
Hydrocotarnine may be prepared from all the solutions obtained in the purification of cotarnine, and directly from the crude cotarnine-solution filtered from the crystals of opianic acid formed at the same time. It is also formed, to the amount of 2 to 5 per cent., in the oxidation of narcotine; hence Beckett a. Wright regard it as an original product of the decomposition of narcotine, which is for the most part converted, by further oxidation, into cotarnine. It may in fact be converted into cotarnine by the action of ferric chloride, of potassium dichromate and sulphuric acid, or of manganese dioxide and sulphuric acid, the cotarnine obtained with the first of these reagents being very nearly pure.

Narcotine treated with *zinc and dilute hydrochloric acid* is completely converted into hydrocotarnine (m. p. $54^\circ\cdot5$) and meconin, without any formation of opianic acid. Narcotine heated to boiling with a quantity of *baryta-water* sufficient to form a clear solution, gave off methylamine, and the solution was found to contain *meconin*, but no cotarnine, hydrocotarnine, or opianic acid. When narcotine was heated with water in sealed tubes to 140° - 150° , hydrocotarnine in small quantity could be detected if the heating had been continued only for 6 or 7 hours, but not a trace when the heating was prolonged for 21 to 28 hours. In the latter case 20 per cent. of meconin was obtained, and a smaller quantity after heating for a shorter time.

From these results Beckett a. Wright infer that the older equations



do not explain with sufficient simplicity the facts hitherto known, but that a much more satisfactory explanation is afforded by the equations proposed by Hesse, viz.:



The fact that Anderson, by acting on narcotine with nitric acid, obtained meconin, may be reconciled with the results above stated, if it be supposed that the meconin was formed from opianic acid, a reaction indeed actually observed by Matthiessen a. Foster:



Hydrocotarnine Ethiodide, $C^{12}H^{13}NO^3 \cdot C^2H^5I$, is formed by heating hydrocotarnine to 100° with excess of ethyl iodide and absolute alcohol, and crystallises from alcoholic solution on cooling in anhydrous white micaceous plates slightly soluble in water, more freely in alcohol, especially at the boiling heat. When agitated with water and

silver oxide, it yields an alkaline liquid which precipitates metallic salts, especially those of mercury and silver, rapidly absorbs carbonic acid from the air, and then yields on evaporation crystals of hydrocotarnine ethylcarbonate, $(C^{12}H^{13}NO^3.C^2H^5)^2CO^2 + 4H^2O$, which are soluble in water and in alcohol, but not in ether.

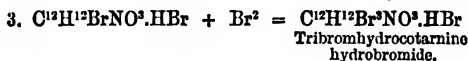
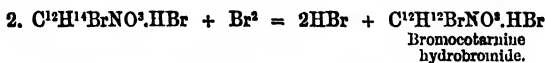
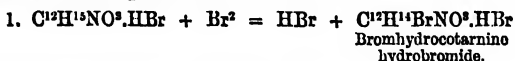
The ethiodide, agitated with water and recently precipitated silver chloride, is converted into the ethylochloride, $C^{12}H^{13}NO^3.C^2H^5Cl$, which forms feathery crystals, melts at 100° to a vitreous mass solidifying in the crystalline form on cooling, and yields a platinochloride, $(C^{12}H^{13}NO^3.C^2H^5Cl)^2PtCl^4$. The ethiodide is not altered by heating with excess of ethyl iodide.

Narcotine, heated as above with ethyl iodide and absolute alcohol, yields an amorphous, easily decomposable ethiodide, $C^{22}H^{13}NO^7.C^2H^5I$, convertible like the preceding into chlorine- and hydroxyl-compounds, which are also easily decomposable.

Cotarnine forms an amorphous very hygroscopic ethiodide, convertible into an amorphous hydroxyl-derivative. The corresponding ethylochloride and platinum salt are likewise amorphous.

Acetic anhydride does not act upon either narcotine, cotarnine, or hydrocotarnine.

Bromine-derivatives of Cotarnine and Hydrocotarnine (Wright, *Chem. Soc. J.* xxxii. 525).—Hydrocotarnine hydrobromide treated with bromine yields the following products of decomposition:—



The formation of the first two of these bodies is preceded by that of the unstable addition-products, $C^{12}H^{13}Br^2NO^3.HBr$ and $C^{12}H^{14}Br^2NO^3.HBr$. The third addition-product, tribromhydrocotarnine hydrobromide, forms well-defined permanent crystals.

Bromhydrocotarnine and bromocotarnine are similar in their general properties to hydrocotarnine and cotarnine respectively. The former is anhydrous, and melts at 76° ; the latter has the composition $C^{12}H^{12}BrNO^3 + H^2O$, and gives off its water at 100° with decomposition. Its hydrobromide, $C^{12}H^{13}BrNO^3.HBr + H^2O$, crystallises well, and dissolves easily in water. The hydrobromide of bromhydrocotarnine is anhydrous and sparingly soluble in water.

When bromocotarnine hydrobromide is heated above 200° it melts, gives off hydrogen bromide, and a combustible vapour (probably CH^3Br), and forms a small quantity of the bromide of a new base, $C^{11}H^8NO^3$, called tarconine, together with an indigo-blue substance which is the hydrobromide of the base $C^{20}H^{14}N^2O^6$. These two bases and their salts are insoluble in water, ether, alcohol, benzene, carbon sulphide, and petroleum, slightly soluble at the boiling heat in aniline and glacial acetic acid, with which they form dark blue solutions. Strong sulphuric acid dissolves them, forming with the latter the sulphate $(C^{20}H^{14}N^2O^6)^2H^2SO^4$, the solution of which has a colour like that of magenta, equally beautiful and possessing great tinctorial power.

Tribromhydrocotarnine Hydrobromide melts at 200° , and is at the same time resolved into hydrogen bromide, methyl bromide, and bromotarconine hydrobromide, as shown by the equation



Bromotarconine forms slender scarlet crystals, $C^{11}H^8BrNO^3.2H^2O$, which when heated to 100° give off their water and assume a crimson colour, and retain that colour if immediately recrystallised from perfectly anhydrous alcohol, but crystallise out with scarlet colour if the slightest trace of moisture is present. The salts of bromotarconine have a faint-yellow colour, crystallise well, and dissolve sparingly in cold water. The hydrobromide and hydrochloride crystallise each with $2H^2O$.

Cotarnine Hydrobromide, $C^{12}H^{13}NO^3.HBr + 2H^2O$, is very soluble in water, and forms with bromine the addition-product, *dibromhydrobromocotarnine hydrobromide*, $C^{12}H^{13}Br^2NO^3.HBr$, which, when further treated with bromine, yields tribromocotarnine hydrobromide identical with that which is formed from hydrocotarnine. By the action of water, dibromhydrocotarnine hydrobromide is resolved into hydrobromic acid and bromocotarnine hydrobromide. Bromocotarnine treated with zinc and hydrochloric acid takes up 2 at. hydrogen and is converted into bromhydrocotarnine, identical with that which is formed from hydrocotarnine.

Oxynarcotine, $C^{22}H^{23}NO^3 = N \equiv [C^{11}H^{11}(CH^3)O^3].CO.C^6H^5 \begin{Bmatrix} COOH \\ (OCH^3)^2 \end{Bmatrix}$. This base,

of which narcotine may be regarded as the aldehyde, was obtained by Beckett & Wright (*Chem. Soc. J.* xxix, 461) from crystals which remained undissolved in the process of purifying narceine. It probably does not exist in opium ready-formed, but is formed from narcotine by the action of atmospheric oxygen. To purify it, the crude base is treated with the exact quantity of sulphuric acid required to dissolve it; the solution is treated with the exact quantity of caustic soda required to precipitate the base; the precipitated crystals, forming a mass very much like paper-pulp, are repeatedly boiled with water, which takes up admixed narceine and finally leaves sandy crystals which must be repeatedly boiled with alcohol; and the base thus far purified is finally converted into the hydrochloride, and precipitated in the pure state by addition of a slight excess of caustic potash. By applying the same treatment to the mother-liquors obtained in the separation by water, as above described, it is easy to effect the separation of the oxynarcotine from the narceine.

Oxynarcotine is but sparingly soluble in water and in alcohol even when hot, and nearly insoluble in benzene and in chloroform. It is precipitated from the solutions of its salts by the fixed alkalis and their carbonates, but redissolved by an excess of the precipitant. Its solution in hot hydrochloric acid yields soft crystals of the hydrochloride, $C^{22}H^{23}NO^3.HCl + 2H^2O$, which become anhydrous at 100° , and are resolved by boiling with water into basic salt and acid.

By oxidation with ferric chloride and other reagents, oxynarcotine is resolved into hydrocotarnine and hemipinic acid:



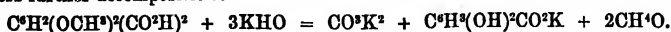
without formation of opianic acid. It is decomposed by heating with water in a sealed tube to 140° – 150° for 15 to 20 hours, but the product does not contain opianic acid, hemipinic acid, meconin, or any alkaloïd soluble in ether (Beckett & Wright).

Hemipinic and Opianic Acids. Orientation of Narcotine-derivatives.

Hemipinic acid, $C^{10}H^{10}O^6$, was obtained, together with meconin, by fusing opianic acid with three times its weight of potassium hydroxide, the two being separated by Matthiessen & Foster's process (iii, 142). The meconin thus obtained fused at 102° – 102.5° . Crude hemipinic acid, partially purified by conversion into the lead salt, always contains small quantities of methylnormeconin, $C^6H^5O^4$, which gives a blue coloration with ferric chloride, and is difficult to separate by recrystallisation, but may be easily removed by oxidation with chromic acid mixture. Pure hemipinic acid may also be obtained by washing its ammonium salt, dried at 100° , with alcohol, dissolving it in hydrochloric acid, and extracting with ether. Hemipinic acid, heated for an hour to 180° and crystallised from alcohol, is converted into hemipinic anhydride, which forms shining needles melting at 166° – 167° (corr.) The acid containing methylnormeconin melts at 10° – 15° , and its anhydride at 6° – 7° . The ease with which hemipinic acid is converted into the anhydride points to the conclusion that it belongs to the phthalic series—in other words, that it is an ortho-compound.

Sodium hemipinate heated in a retort with twice its weight of soda-lime yielded, together with a watery distillate, a heavy oil boiling at first between 200° and 210° , but after two rectifications between 204° and 206° (corr.) This oil is identical in all its reactions with the dimethylpyrocatechin, $C^6H^4(OCH^3)_2.OH$, which Marasse obtained from beech-tar creosote (vi, 504), and is resolved by heating with hydriodic acid into methyl iodide and pyrocatechin.

Hemipinic acid heated with six to seven times its weight of potassium hydroxide and a little water to 200° – 220° —the temperature rising in about fifteen minutes to 235° – 240° —is converted into protocatechuic acid, $C^6H^3(OH)^2.CO^2H + H^2O$ [$CO^2H : OH : OH = 1 : 3 : 4$]. Hence hemipinic acid may be regarded as carboxylated dimethylpyrocatechuic acid, $C^6H^2(CO^2H)^2(OCH^3)^2$, in which the two carboxyl-groups are probably in the positions 1, 2, the methoxyl-groups in 3, 4 or 4, 5. By heating with soda-lime, it is converted into $2CO^2$ and $C^6H^4(OCH^3)^2$; by heating alone into the anhydride $C^6H^2(OCH^3)^2 \begin{Bmatrix} CO \\ CO \end{Bmatrix} O$; and by fusion with potassium hydroxide, into carbonic acid, protocatechuic acid, and methyl alcohol, which suffers further decomposition:



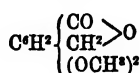
Hemipinic acid cautiously heated with hydriodic acid is converted into methyl-norhemipinic acid, $C^6H^5O^6 + 2H^2O$, which gives off its water at 100° , with partial decomposition. It is very unstable, as are also its salts; melts with decomposition at 150° – 155° , and is identical with Liechti's *isopinic acid* (vi, 882), to which however Liechti assigned a different formula.

Methylnorhemipinic acid, fused with potassium hydroxide at 240° , till a sample no longer gives a blue colour with ferric chloride, is converted into protocatechuic acid; when heated above its melting point, it gives off carbon dioxide; and when distilled with pumice-powder it yields methylprotocatechuic acid (m. p. 249° corr.), together with an oily substance, probably guaiacol. Methylnorhemipinic acid, heated for half an hour to 160° – 170° , yields an acid which may be purified by conversion into the ammonium salt, dissolves easily in hot, sparingly in cold water, is coloured blue-violet by ferric chloride, and is perhaps identical with Liechti's *opinic acid*. When heated with dilute hydrochloric or hydriodic acid, it yields methylprotocatechuic and protocatechuic acid.

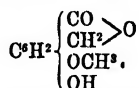
Hemipinic acid, heated for ten hours with excess of strong hydrochloric acid, yields *monomethylprotocatechuic acid*, melting at 251° (corr.) (comp. Matthiessen a. Foster, *Chem. Soc. J.* xvi. 354). This acid yields a dimethyl-derivative which is identical with *dimethylprotocatechuic acid*, but, contrary to Kölle's statement (vii. 432), crystallises with 1 mol. $H^{\circ}O$.

Meconin, fused with potassium hydroxide, yields methylnormeconin, $C^8H^8O^4$, as an anhydrous crystalline body, which melts at 125° , and is turned blue by ferric chloride. The same compound is produced in like manner from narcotine. By further fusion with potash, it is converted with evolution of hydrogen into protocatechuic acid.

Meconin and methylnormeconin may be represented by the following formulæ:



Meconin.



Methylnormeconin.

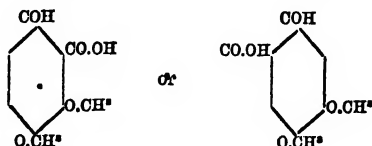
Hypogallic acid is regarded by Beckett a. Wright as a mixture of opianic and hemipinic acids, probably with addition of protocatechuic acid (p. 1083).

Reactions of Opianic Acid.—Sodium opianate, mixed with soda-lime (caustic baryta yields a smaller product), dried at 130° – 140° , and distilled in a retort, yields, together with a watery distillate, a heavy oil, the portion of which boiling above 260° contains a fraction which passes over at 280° – 285° (uncorr.), and solidifies in a freezing mixture to a mass which melts at 41° . On one occasion, the whole of the crude products distilled over at 260° , but mostly the greater part passed over below 200° . The oil has the composition $C^8H^{10}O^3$, and agrees in all respects, except its melting point, with Tiemann's methyl-vanillin (p. 306). When heated with very dilute sulphuric acid, with gradual addition of potassium dichromate, it yielded a small quantity of an acid which melted at 171° , gave no colour-reaction with ferric chloride, and when heated to 220° with potassium hydroxide, was converted into an acid exhibiting the reactions of protocatechuic acid. This oxidation-product of methyl-vanillin is therefore doubtless dimethylprotocatechuic acid.

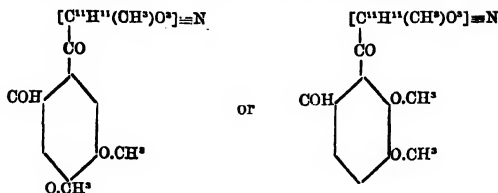
When methyl-vanillin is heated for ten hours with strong hydrochloric acid, methyl chloride is formed, and the liquid on cooling deposits a dark-coloured tar; and on dissolving this in ether, agitating the solution with caustic potash, separating the dark-coloured alkaline liquid, acidifying with hydrochloric acid, exhausting with fresh ether, and evaporating the ethereal solution, an oily residue is left, which on standing yields crystals having the composition $C^8H^{10}O^3$, smelling like vanilla, sparingly soluble in cold, easily in hot water, melting at 80° , and identical in every respect with Tiemann a. Haarmann's vanillin. The quantity of vanillin thus obtained is, however, very small, so that the preparation of this substance from opium is not likely to be successful as a commercial operation.

The formation of dimethyl-protocatechuic aldehyde by the action of heat on a mixture of sodium opianate and soda-lime shows that the $COOH$ radicle eliminated from opianic acid by the action of soda-lime is in the same position as that removed from hemipinic acid by the action of caustic potash at 240° .

From the character of the alternative formulæ thus deducible for opianic acid, viz.:



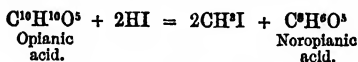
it follows that narcotine must have one of the two structures :



the CO-group which links the benzene radicle to the cotarnine nucleus, corresponding in position with the CO.OH eliminated from opianic acid by soda-lime, and with that removed from hemipinic acid by heating with potash at 240° .

Opianic acid, treated with hydrochloric acid gas, is resolved, according to Matthiesen a. Foster (vi. 882), into methyl chloride and methylnoropianic acid, $\text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}}$, which, when distilled with soda-lime, might be expected to yield vanillin; experiment shows, however, that a more thorough decomposition takes place, the greater part of the opianic acid being completely charred.

Opianic acid, treated with a large quantity of *hydriodic acid*, yields nearly the theoretical amount of methyl iodide, in accordance with the equation :



The noropianic acid crystallises with $2\text{H}^{\text{H}}\text{O}$, and is isomeric with that obtained by Tiemann (*infra*).

Isopianic and Isohemipinic acids, and other acids related to them, isomeric with those just described as derived from narcotine, have been obtained by Tiemann a. Mendelssohn (*Deut. Chem. Ges. Ber.* x. 393), starting from aldehydovanillic acid, $\text{C}^{\text{H}^{\text{H}}}\text{O}^{\text{H}}$, which, as already observed (p. 291), has the structure represented by the

formula $\text{C}^{\text{H}^{\text{H}}}\text{C}^{\text{H}^{\text{H}}}\text{H}.\text{C}(\text{OH})_2.\text{CH}(\text{OCH}^{\text{H}}).\text{CO}(\text{OCH}^{\text{H}}).\text{H}$. The acids thus obtained belong to the isophthalic series; those obtained from narcotine, to the phthalic series. With regard to aldehydovanillic or methylnorisopianic acid, Tiemann a. Mendelssohn observe that its aqueous solution does not reduce either silver nitrate or Fehling's solution at the boiling heat. It forms two series of salts. The *potassium, sodium, and ammonium* salts are soluble in water, the solution having a characteristic yellow colour. From a strongly ammoniacal solution of the acid, barium and calcium chlorides throw down slightly soluble (possibly basic) *barium and calcium salts*; and the acid, neutralised with ammonia, forms with silver nitrate a yellowish-white *silver salt*; with cupric sulphate, a green *copper salt*, soluble with green colour in excess of ammonia. A crystalline *lead salt* is precipitated from the aqueous solution of the acid by lead acetate, the precipitate increasing on addition of ammonia.

The mono- and di-methylic ethers of methylnorisopianic acid are formed simultaneously by digesting 1 mol. of the acid at 100° with 2 mols. KIO , methyl alcohol, and excess of methyl iodide, and may be separated from one another by agitating their ethereal solution with a very dilute alkaline ley. The monomethylic ether or *methylic methylnorisopianate*, $\text{C}^{\text{H}^{\text{H}}}\text{C}(\text{COH})(\text{OH})(\text{OCH}^{\text{H}})(\text{COOCH}^{\text{H}})$, is precipitated from the alkaline solution on acidulation in flocks of yellow needles, which, after recrystallisation from water, melt at 134° – 135° , and dissolve in solution of sodium carbonate, but without evolution of carbon dioxide. The dimethylic ether or *methyl isopianate*, $\text{C}^{\text{H}^{\text{H}}}\text{C}(\text{COH})(\text{OCH}^{\text{H}})_2(\text{COOCH}^{\text{H}})$, is obtained by spontaneous evaporation of the ethereal solution, in the form of an oil, which soon solidifies to a crystalline mass. When recrystallised from boiling water, in which it is but slightly soluble, it forms slender, white felted needles, having a characteristic aromatic odour, and melting at 98° – 99° .

Isopianic acid, $\text{C}^{\text{H}^{\text{H}}}\text{C}(\text{COH})(\text{OCH}^{\text{H}})_2(\text{COOH})$, obtained from the dimethylic ether by boiling with alkalis, crystallises from boiling water in slender white needles, melting at 210° – 211° (uncorr.), and dissolves readily in alcohol and in ether. In strong sulphuric acid it dissolves with deep yellow colour, in alkalis without coloration: no colour-reaction with ferric chloride. With *sodium bisulphite* it forms a sparingly soluble compound. The isopianates of ammonia and the fixed alkalis are easily soluble in water. The solution of the ammonium salt is not precipitated by chloride of barium or calcium. Cupric sulphate precipitates from it a bluish-white *copper salt*, soluble with blue colour in excess of ammonia; lead acetate forms a sparingly soluble *lead salt*; silver nitrate, a white *silver salt*, which may be crystallised from hot water

without decomposition. By oxidation with dilute solution of potassium permanganate, at 70°, isopianic acid is converted into isohemipinic acid (*infra*).

Isonoropianic or *Aldehydoprotocatechuic acid*, $C^6H^2(COH)(OH)^2COOH$, is produced by heating aldehydovanillic acid with dilute hydrochloric acid to 170°–180°, and crystallises from hot water in yellowish needles, which melt at a temperature above 240°, dissolve without much difficulty in cold water, easily in hot water, alcohol, and ether. The aqueous solution, mixed with an alkali, immediately turns yellow, and after long standing or after heating, reddish-yellow; with ferric chloride it produces a dark-green colour, suddenly changing to reddish-violet on addition of alkalis. It reduces Fehling's solution at the boiling heat; silver nitrate only on addition of ammonia. Hence it follows that isonoropianic acid is not identical, but isomeric, with Hlasiwetz's quercimeric acid (v. 5).

Isohemipinic acid, $C^6H^2(OCH^3)^2(COOH^2)$, formed, as above mentioned, by oxidising isopianic acid with a dilute solution (1 : 5) of potassium permanganate at 70°, crystallises from hot water in white needles which dissolve easily in alcohol and ether, without much difficulty in hot water, but are nearly insoluble in cold water. It melts at 245°–246°, and sublimates at a higher temperature without formation of anhydride. It is bibasic. The *potassium, sodium, ammonium, barium, and calcium* salts are easily soluble and crystallise well. The ammonia salt, neutralised with an acid, yields with copper sulphate, a bluish-white *copper salt*, with lead acetate, a white *lead salt*, and with silver nitrate, a white *silver salt* which dissolves in hot water without alteration (Tiemann a. Mendelsohn).

NATROLITE. See ZEOLITES.

NECTAR. This name is applied to the sweet-tasting fluid secreted within the cups of insect-fertilised flowers. On the amounts of cane- and fruit-sugar contained in the nectar of various flowers, see A. S. Wilson (*Chem. News*, xxxviii. 93; *Chem. Soc. J.* xxxiv. 997).

NEFIEDEWITE. This name is given by P. Pusirewsky (*Jahrb. f. Min.* 1873, 420) to a white to rose-red amorphous substance resembling lithomarge, occurring, together with fluor spar, in limestone at Nertschinsk in Siberia. Hardness = 1.5. Sp. gr. = 2.335 at 18°. The substance gives off 11.13 per cent. water over sulphuric acid, 19.13 at 250°, and 4.73 at a still higher temperature. A certain proportion of it (0.2 per cent.) dissolves in water with alkaline reaction (Na^2O), and may be regarded as an admixture. Pusirewsky assigns to this substance the formula $H^1MgAl^2Si^3O^{16}$, but the analyses from which he deduces this formula differ considerably from one another.

NEGRO COFFEE. The seeds of *Cassia occidentalis*, from the French colonies in Africa, are known by this name. According to an analysis by J. Clouet (*Pharm. J. Trans.* [3], vi. 909) they contain in 100 pts.:

Fat (Olein and Margarín)	4.9
Tannic acid	0.9
Gum	28.8
Sugar	2.1
Starch	2.0
Cellulose	34.0
Water	7.0
Calcium sulphate and phosphate, Chrysophanic acid	0.9
Malic acid, Sodium chloride, Magnesium sulphate, Iron,	
Silica	5.4
Achrosin	13.58

Achrosin, perhaps a mixture of several substances, is extracted from the seeds by alcohol. The seeds have a purgative action, and are used as a remedy for fever. They lose their purgative properties by roasting, and an infusion of the roasted seeds smells and tastes like one of roasted coffee-beans.

NEOCHEYSOLITE. A mineral found in the cavities of the Vesuvian lava of 1631. It is crystallographically identical with olivine, and differs from it chemically only by its higher amounts of iron and manganese, which replace nearly the whole of the magnesium (A. Scacchi, *Zeitschr. Kryst.* ii. 104).

NEOGEN. An alloy containing:

Cu	Zn	Ni	Sn	Al	Bi
58	27	12	2	0.5	0.5 = 100

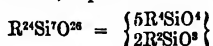
To prepare it the constituent metals are separately fused and very carefully triturated together (Sauvage, *Dingl. pol. J.* ccxv. 377).

NEOLITE. According to Frenzel (*Jahrb. f. Min.* 1874, 676) the crust of the Freiberg pseudomorphs of iron pyrites and magnetic pyrites is a mineral nearly related to neolite, and having the composition A. The values B are calculated from the formula $4\text{FeO} \cdot \text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 3\text{H}_2\text{O}$:

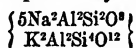
SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	CaO	MgO	H ^a O	
22.28	16.82	2.44	41.19	4.23	1.82	1.31	8.88	= 98.97
21.25	18.20	—	50.99	—	—	—	9.56	= 100

NEPHELIN. On nephelin from Lätium, J. Strüver (*Zeitschr. Kryst.* i. 240) observed the forms 0P , ∞P , ∞P_2 , ∞P_3 , $\frac{1}{2}\text{P}$, 2P , 2P_2 . The measurements agreed well with those of nephelin from Somma (iv. 31). The crystals, which are mostly colourless, white, or grey, rarely green or flesh-coloured, occur in geodes of the lavas and ejected blocks.

Rammelsberg (*Berl. Akad. Ber.* 1876, 695) discusses the chemical constitution of nephelin on the basis of new analyses (1-4) of Vesuvian nephelin, the only material sufficiently definite in composition to be available for the decision of the question. He assumes the formula $\text{R}^{\text{K}}(\text{Al}^{\text{N}})_2\text{Si}^{\text{O}}\text{O}^{\text{S}}$, which, accordingly as $\text{K} : \text{Na} = 1 : 5$ or $1 : 6$, gives the values (5) or (6) (*infra*), the lime present being attributed to admixture of augite and garnet. According to this, nephelin should be represented by the formula:



For $\text{K} : \text{Na} = 1 : 5$, the formula of nephelin may also be written in the form:



the first member of which is the silicate occurring in sodalite, &c., and the second leucite:

	SiO ^a	Al ^a O ^a	Na ^a O	K ^a O	CaO	Total	Sp. gr.
1 (found)	44.77	34.94	15.33	4.47	0.50	100.01	2.600
2 "	44.88	34.37	15.40	4.87	0.54	100.06	
3 "	44.63	34.39	15.31	4.93	0.67	99.93	to
4 "	45.65	34.27	16.35	4.32	trace	100.59	2.6087
5 (calc.)	45.17	33.10	16.67	5.06	—	100	
6 "	45.28	33.19	17.17	4.36	—	100	

See also H. Rauff (*Jahrb. f. Min.* 1878, 745; *Chem. Soc. J.* xxxvi. 606).

For distinguishing between nephelin and apatite in a microscopic section of a rock, the following reactions are given by A. Streng (*Jahrb. f. Min.* 1877, 94): Nephelin is decomposed by very strong hydrochloric acid, the cavities of the etched crystals becoming gradually filled with cubes of sodium chloride; apatite, treated with a concentrated solution of ammonium molybdate in nitric acid, yields small yellow octohedrons and rhombic dodecahedrons, which spread over the entire field of view, excepting the part occupied by the apatite itself, at which the reaction is prevented by the excess of phosphoric acid present.

Nephelin picrite is the name given by E. Boricky (*Jahrb. f. Min.* 1877, 539) to a rock from the Devine near Wartenberg in Bohemia, distinguished from Tschermak's picrite by the constant presence of nephelin and perowskite, the latter mineral forming sharp-edged crystals, 0.01 to 0.02 mm. in diameter.

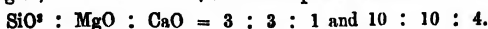
On the nephelin-rock of Meiches in the Odenwald, see v. Klipstein (*Jahrb. f. Min.* 1878, 722; *Chem. Soc. J.* xxxvi. 607).

NEPHRITE. Four nephrites, collected by H. v. Schlagintweit in Central Asia, have been analysed by L. R. v. Fellenberg (*Münch. Akad. Ber.* iii. 277). They were found imbedded in gneiss in clefts in the neighbourhood of Gulbashén, a halting place on the right side of the river Karkash, in the Künlün range, lat. $36^\circ 13' \text{N}$, long. $78^\circ 16' \text{E}$. of Greenwich, at a height of 3725 met.:

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	MnO	CuO	MgO	K ^a O	SiF ^a	H ^a O	
1.	59.30	0.53	—	0.70	0.55	10.47	25.64	1.02	1.28	0.62	= 100.11
2.	59.50	0.75	—	1.35	0.79	11.60	24.24	1.57	—	0.85	= 100.65
3.	58.42	0.70	—	0.67	0.46	13.85	24.39	0.10	0.60	1.20	= 100.39
4.	59.21	0.50	0.34	0.97	0.53	14.61	23.55	0.19	—	0.78	= 100.68

Sp. gr. of 1 = 2.972 at 44° ; of 2 = 2.957 at 75° ; of 3 = 2.980 at 17° ; of 4 = 2.974 at 20° .

The analyses give, for silica = SiO_2 , values comprised between the limits:



These nephrites, when first removed from the bed, are soft enough to be easily worked, whereas older specimens have a hardness of 6.5.

H. Fisher (*Min. Mitth.* 1873, 155) describes the breaking up of a refractory block of nephrite by ignition and rapid cooling, and is of opinion that this mode of treatment, which is known to be adopted for the disintegration of other hard minerals, may throw light on the working of nephrite in prehistoric times.

NEPTUNIUM. See NIOBIUM.

NEURINE. According to J. Mauthner (*Liebig's Annalen*, clxxv. 178) an aqueous solution of neurine dissolves blood-fibrin to a clear liquid which does not blacken lead acetate, is not precipitated by alcohol, but yields a precipitate of fibrin on gradual addition of an acid. On the putrefactive decomposition of neurine in the bile, see p. 324.

NICKEL. *Occurrence.*—Metallic nickel occurs to the amount of 0·75 per cent. in the magnetic platinum ore of Nischne-Tagilsk in the Ural (Terreil, *Compt. rend.* lxxxii. 1116).

On the sulphide of nickel and iron, $4\text{Fe}^2\text{S}^3 \cdot \text{Ni}^2\text{S}^3$, occurring at Horbach in the Schwarzwald, see HORBACHITE (p. 1041).

Statistical reports of the extraction of nickel from its ores in Europe and America are given in the *Hannoversches Wochenblatt für Handel und Gewerbe*, 1873, No. 36; *Dingl. pol. J.* ccx. 75; *Jahresb. f. Chem.* 1873, 994. On the Metallurgy of Nickel, see also Lundborg (*Dingl. pol. J.* ccxxvi. 643).

Coating of other Metals with Nickel.—*Electrodeposition.*—A nickel-bath, much used for this purpose in France, is prepared by dissolving 4 pts. nickel nitrate in 4 pts. aqueous ammonia and 150 pts. water holding in solution 50 pts. acid sodium sulphite. With the aid of a very feeble current, the deposition is completed in a few minutes. There is no necessity for interrupting the process in order to clean the surface and thereby insure the desired thickness of the deposit, the nickelled objects merely requiring to be dried in sawdust (Boden, *Dingl. pol. J.* ccxvii. 256). Another nickel-bath consists of 87·5 pts. nickel sulphate, 20 ammonium sulphate, 17·5 nitric acid and 2 litres of water (Hesse, *ibid.*) Martin a. Delamotte dissolve 1250 grams of citric acid, 500 sal-ammoniac (or ammonium sulphate), and 500 ammonium nitrate in 15 litres of water; heat the solution to 80° C. and saturate it gradually with recently precipitated nickel hydrate; then add 2·5 litres of aqueous ammonia; dilute to 25 litres; and after cooling, add 500 grams of ammonium carbonate; leave the precipitate to settle, and filter the liquid. The solution thus obtained contains about 50 grams of nickel in the litre, and has a density of 11° B. The nickel may be conveniently precipitated from it at 50°. The addition of potash or soda renders it possible to obtain thicker electro-deposits of nickel. See also O. Silvestri (*Ber.* x. 889) and A. Kayser (*Chem. Centr.* 1878, 127; *Chem. Soc. J.* xxxiv. 537).

On the coating of Iron with Nickel, see p. 1118.

Malleable Nickel.—The addition of magnesium in the proportion of $\frac{1}{8}$ per cent. to nickel or cobalt renders the metal malleable and ductile, and susceptible of a high polish. The alloy does not alter in the air, and is well fitted for making harness, &c. It can be welded to iron or steel at a white heat, and rolled into thin plates without separating therefrom. It is prepared by dropping the magnesium through a hole in the cover of a crucible in which the nickel or cobalt is heated, a few pieces of charcoal having been previously introduced to remove oxygen (J. Fleitmann, *Ber.* xii. 454).

On the Magnetic relations of Nickel, see MAGNETISM (p. 1248).

On the Manufacture of large Castings of Nickel, see Winckler (*Dingl. pol. J.* ccxxii. 175; *Chem. Soc. J.* xxxi. 238).

Detection.—To distinguish between nickel, cobalt, manganese, and zinc, A. H. Allen (*Chem. News*, xxiii. 290) adds potassium ferricyanide in excess to an ammoniacal solution of the metal containing ammonium chloride. Manganese then gives a brown precipitate; cobalt, dark red; nickel, copper-red in a hot solution, no precipitate in the cold; zinc, no precipitate either in hot or in cold solution.

R. H. Davies (*ibid.* xxxii. 44) modifies this method by adding ferrocyanide as well as ferricyanide of potassium, or the ferrocyanide alone. On adding the ferricyanide to a solution of nickel and cobalt till the resulting precipitate is redissolved, and then the ferrocyanide, a precipitate of nickel ferrocyanide is obtained, especially if the ammonia has previously been partly neutralised by a few drops of hydrochloric acid. The cobalt being more soluble is not thrown down till a larger quantity of acid has been added, whereupon the red-brown colour of the solution disappears, and a yellowish-white precipitate of cobalt ferrocyanide is produced. The same result is obtained when ferrocyanide alone is employed. Nickel may also be easily recognised by the greenish colour produced on adding the ferrocyanide to its solution, even when

extremely dilute, this colour being very different from that which is produced in like manner by traces of ferrous salts.

Estimation by Electrolysis (A. Riche, *Ann. Chim. Phys.* [5], xiii. 508).—Nickel may be rapidly and accurately estimated by decomposing its salts either in an acid or in an alkaline solution, and weighing the precipitated metal. The apparatus used consists of a platinum crucible in which is suspended a hollow truncated cone of platinum with small openings in the side: this cone serves as the negative pole, the crucible forming the positive pole. The decomposition may take place at the ordinary or at a higher or lower temperature. From a solution slightly acidulated with sulphuric acid at 60°–80° nickel may be precipitated by a current of two Bunsen's cells. The precipitation is generally complete the first time, but to ensure accuracy, it is always advisable to subject the solution to the current a second time.

The same method may be applied to the analysis of alloys of nickel.

Nickel and Copper.—Only the copper is deposited when an acid (sulphuric or nitric acid) solution is subjected to the action of one Bunsen's element; the solution containing the nickel is made alkaline with ammonia, and then slightly acid; on passing the current the nickel is deposited.

Nickel and Lead.—The lead is first precipitated as dioxide from a nitric acid solution by means of a Leclanché's element, and the nickel is determined afterwards.

Nickel and Manganese.—The nickel is completely precipitated on the negative pole when a current is passed through an acid (sulphuric acid) solution, and may be washed and weighed. The action is then continued, if necessary, until the manganese is completely precipitated as dioxide on the positive pole.

Nickel and Magnesium.—The separation is effected in a solution made acid with sulphuric acid.

G. P. Schweder (*Zeitschr. anal. Chem.* 1877, 344) recommends that the nickel be precipitated by a powerful current from a strongly ammoniacal solution not containing much sal-ammoniac—iron, if present, having been previously precipitated as basic ferric sulphate.

On the analysis of Nickel Coins by the Electrolytic method, see E. Busse (*Zeitschr. anal. Chem.* xvii. 53; *Chem. Soc. J.* xxxiv. 338).

Estimation of Nickel in Pyrrhotites and Mattes.—The following method of determining nickel in these substances is based upon the fact that nickel phosphate is completely soluble, while phosphate of iron is almost insoluble, in acetic acid in the presence of an excess of sodium phosphate.

The ore is dissolved in hydrochloric acid, with addition of a little nitric acid; the solution is treated with hydrogen sulphide and filtered; the filtrate boiled; the iron oxidised with nitric acid; and ammonia is added until a permanent precipitate begins to form. Acetic acid is then added until the precipitate is redissolved. To this boiling hot solution a hot concentrated solution of ordinary sodium phosphate is added in excess, and the nearly white precipitate is filtered off and washed with hot water containing acetic acid. The filtrate is heated nearly to boiling, and caustic potash added until the odour of ammonia is distinctly perceptible. The apple-green precipitate of nickel phosphate is partially washed and dissolved in a little dilute sulphuric acid; the solution rendered strongly alkaline by ammonia; and the nickel precipitated by the battery. If more than 3 per cent. of nickel is present, the precipitate of iron phosphate must be redissolved and treated as before, as it may contain a little nickel (Margaret S. Cheney a. Ellen S. Richards, *Sill. Am. J.* [3], xiv. 178).

Separation of Nickel from other Metals.—Wöhler's method of separating nickel (and cobalt) from arsenic, without the use of hydrogen sulphide, has already been described under COBALT (p. 541); also Phipson's method, which consists in precipitating the two metals together as xanthates, and dissolving up the nickel salt with dilute ammonia. According to A. Guyard (*Chem. News*, xxxiv. 255), recently precipitated nickel sulphide dissolves very readily in very dilute solutions of *alkaline cyanides*, whereas cobalt sulphide does not, so that this reaction may be used for the quantitative separation of the two metals. For this purpose, the recently precipitated sulphides are suspended in water, and a very dilute solution of potassium cyanide is added in slight excess. The whole of the nickel then remains in solution, and may be precipitated as cyanide by dilute sulphuric or hydrochloric acid. The insoluble cobalt sulphide, after filtration and washing, is perfectly pure.

From iron, in the form of ferric salt, nickel may be separated by adding to the solution a quantity of *ammonia* not sufficient to precipitate all the iron as ferric oxide, and then *acetic acid*. From the clear solution thus obtained, the whole of the iron may be precipitated by sodium phosphate, and the nickel estimated in the filtrate (M. S. Cheney a. E. S. Richards, *Sill. Am. J.* [3], xiv. 178).

From zinc, nickel may be separated by evaporating the solution mixed with *sal-ammoniac* to dryness, and gradually heating the residue till all the *sal-ammoniac* and all the zinc chloride are volatilised. No loss of nickel is likely to occur (R. Fresenius, *Zeitschr. anal. Chem.* 1873, 66).

Compounds of Nickel.

Nickel may be *amalgamated* in the same way as iron (p. 1097), namely, by placing it, together with some pieces of zinc, in contact with mercury covered with dilute sulphuric or hydrochloric acid (Casamajor).

According to W. A. Ross (*Chem. News*, xxxiv. 150), melting nickel is capable of taking up a large quantity of *silver*, whereas melting silver does not unite with nickel. This difference perhaps depends upon the difference of the melting points of the two metals.

Nickel Arsenide, Ni^3As^2 , obtained by reduction of the arsenate, is a crystalline substance, having a metallic lustre and sp. gr. = 7.71. By fusing with boric oxide, it is converted into Ni^3As , or Ni^4As^2 , which can also be prepared by fusing together a mixture of potassium cyanide, metallic arsenic, and nickel oxide (A. Descamps, *Compt. rend.* lxxxvi. 1065).

Combination with Carbon and Silicon.—According to W. E. Gard (*Sill. Am. J.* [3], xiv. 274), commercial nickel always contains appreciable quantities of carbon and silicon, the latter being probably derived from silica in the charcoal by which the nickel is reduced, or from the crucible. Pure nickel oxide, mixed with half its weight of finely pounded quartz and heated to fusion with charcoal, yielded a white non-metallic regulus of sp. gr. 7.73, and containing 9 to 9.5 per cent. carbon and 6 to 6.2 per cent. silicon. In another experiment, half a pound of granulated commercial nickel was slowly heated to fusion between two layers of charcoal. The metal thus obtained was strongly magnetic, soft, malleable to a certain degree, had a density of 8.04, and contained 2.105 p.c. carbon, of which 2.03 was in the form of graphite, and 0.36 silicon. Nickel and cobalt heated to redness in a stream of *marsh gas* increased perceptibly in weight without exhibiting any actual deposition of carbon; hence it would appear that the carbon entered into chemical combination with the metal. [May not the increase in weight have been due, at least in part, to occluded hydrogen?]

Experiments have also been made by Boussingault (*Compt. rend.* lxxxvi. 509) with the view of ascertaining whether nickel acquires by carburization and tempering the same properties as iron. To determine whether nickel, like iron, takes up carbon by cementation, a plate of nickel was exposed in a cementation furnace from April 25 till March 17; when put in it contained no carbon, but small quantities of iron, arsenic, and copper; when taken out it was perfectly clean, showing no blisters, and possessing the same hardness as before. The plate weighed before cementation 1384 grams; after 1389.25, having gained 5.25, and contained .004 of combined carbon, without a trace of graphite. After being again cemented in a box of sheet iron filled with carbon, it was found by analysis to contain .006 of carbon, which is about the same proportion as in soft steel. By fusing this metal in a crucible lined with charcoal, a button was obtained, containing .0080 of combined carbon, and .0165 graphite; total carbon, .0245. Notwithstanding this high carburization, corresponding to hard steel, the nickel had the same appearance and ductility as before fusion. It is remarkable that the whole carbon taken up by the metal in this last operation was in the state of graphite. A small bar of forged nickel was also cemented, when it contained 98.29 per cent. of nickel, and 0.85 of combined carbon, besides small quantities of iron and silicon. The bar was placed in a clay crucible, surrounded with carbon, and exposed in the hottest part of a cementation furnace for a month; before cementation it weighed 201.907 grams, afterwards 201.857; it therefore lost .050 gram, but notwithstanding this, .504 grams combined carbon, and .303 graphite were taken up. The carbon was in the same form as in tool steel; the bar showed no sign of blistering; it had kept its colour, density, ductility, and softness. From these experiments it would appear that, although nickel combines with carbon, it does not thereby acquire steel-like properties.

On the *Ferrocyanides of Nickel* according to Wyruboff, see CYANIDES (p. 612).

Fluoride, $\text{NiF}^2 \cdot 3\text{H}^2\text{O}$. See FLUORIDES (p. 799).

Mercaptide, $\text{N}(\text{S} \cdot \text{C}^2\text{H}^3)^2$. See MERCAPTIDES (p. 1276).

Oxides. An oxide, Ni^2O^4 , analogous to magnetic iron oxide, is formed by passing oxygen over nickel chloride heated to 350°–440°, the product assuming a blackish colour and giving off chlorine. The change is more quickly effected by moist oxygen, the chlorine being then eliminated in the form of hydrochloric acid, and the chloride being completely transformed in a few hours into a greyish oxide having a metallic aspect, and exhibiting under the microscope crystals having the form of spinel. The

oxide thus formed has no magnetic properties, and is not even attracted by the magnet. It dissolves in hydrochloric acid with evolution of chlorine. When very strongly heated, it gives off 6.6 per cent. oxygen, and is converted into the monoxide NiO , which, when thus prepared, is no longer capable of taking up oxygen and passing to a higher state of oxidation, wherein may be seen an explanation of the well-known fact, that nickel and its salts, when oxidised at high temperatures, never yield an oxide higher than the monoxide (A. Baubigny, *Compt. rend.* lxxxvii. 1082).

A higher oxide, Ni^3O^3 , is precipitated when a solution of a nickel salt mixed with excess of soda is oxidised by sodium hypochlorite. It is very unstable, beginning to decompose as soon as the liquid from which it has been precipitated is decanted off; and when dried in a vacuum over sulphuric acid, it leaves a residue having the composition $\text{Ni}^3\text{O}^{11} \cdot 9\text{H}^2\text{O}$. When the liquid decanted from the oxide Ni^3O^3 is boiled, the salt contained in it is decomposed without formation of stable lower oxides (T. Bayley, *Chem. News*, xxxix. 81).*

A hydrated oxide of nickel and cobalt, called heubachite, is found in thin soot-like deposits, or in the form of dendritic foil and fine globular masses, on clefts in baryta at the St. Anton Mine in the Heubachthal near Wittichen (p. 1029).

A phosphide, Ni^3P^2 , has been prepared by R. Schenk in the same manner as the corresponding iron phosphide. See PHOSPHIDES (vii. 950).

Salts. The following method of preparing pure nickel salts from the commercial metal is given by A. Terreil (*Compt. rend.* lxxix. 1495). The metal, usually containing copper, iron, and small quantities of arsenic, is dissolved in 7 or 8 pts. of aqua regia, the solution is evaporated to dryness, and the residue extracted with water. The solution is then filtered from insoluble iron arsenate, and the filtrate is treated with metallic iron, on which the whole of the copper is immediately deposited. The dissolved iron is then brought to the state of ferric salt by means of chlorine or nitric acid, and the solution is mixed with a quantity of sulphuric acid sufficient to convert all the iron and nickel into sulphates. The hydrochloric acid is next expelled by evaporation to dryness, the residue is redissolved in water, and the iron precipitated at the boiling heat by barium carbonate, which at the same time throws down the last traces of arsenic. The filtrate now contains nothing but nickel sulphate, which by evaporation to dryness may be obtained in a state of perfect purity.

A hydrated nickel-magnesium silicate, from Nouméa, the capital of New Caledonia, examined by A. Liversidge (*Chem. Soc. J.* 1874, 613), occurs, together with chrome-iron ore and steatite, on veins of serpentine, and is traversed by veins of a white silicate, so that it lies in the network like honey in the comb. It has an apple-green colour, is unctuous to the touch, cleaves to the tongue, and splits into small pieces under water. Hardness = 2.5 to 3. The following analyses lead to the formula $10(\text{NiO}, \text{MgO}), 8\text{SiO}_2, 3\text{H}^2\text{O}$:

SiO^2	$\text{Al}^2\text{O}^3, \text{Fe}^2\text{O}^3$	NiO	MgO	CaO	H^2O
47.276	1.560	23.960	21.583	trace	5.212 = 99.591
47.197	1.776	24.060	21.738	trace	5.320 = 100.091

NICOTINE, $\text{C}^8\text{H}^7\text{N}$ or $\text{C}^{10}\text{H}^{14}\text{N}^2$. *Occurrence.*—Heubel maintains—contrary to the statements of Vohl and Eulenberg (vii. 851)—that nicotine is present in tobacco smoke, in the form of a salt which, at high temperatures, is more stable than the base itself. He states that he has detected it both by chemical and by physiological experiments (*Dingl. pol. J.* cvii. 343). According to Preobraschensky (*Russ. Zeitschr. Pharm.* 1876, 705), Indian hemp contains an alkaloid closely resembling nicotine.

Preparation.—W. Kirchmann (*Arch. Pharm.* [3], ix. 209) prepares nicotine by distilling tobacco moistened with solution of sodium carbonate from a tinplate vessel on the water-bath, in a current of carbon dioxide, and collects the alkaloid which passes over in alcohol mixed with sulphuric acid. The colourless solution thus obtained is evaporated to dryness with caustic baryta, and the alkaloid is extracted from the residue by ether.

On the reaction of Nicotine with hydrogen sulphide, see ALKALOIDS (p. 56). On its detection in a mixture of alkaloids, see PLANT-BASES. For the volumetric estimation of nicotine, Zinoffsky adopts the same process as for emetine (p. 732), the number of cubic centimeters of the reagent used being, however, multiplied by 0.00405, instead of 0.189.

* The cobalt oxide, Co^2O^3 , is formed in the same manner as the corresponding nickel oxide, and is somewhat more stable than the latter. When the liquid in which it is formed is boiled, the salt contained in it is decomposed, with evolution of oxygen, and formation of the oxide Co^2O^{11} , intermediate between Co^2O^3 and Co^2O^2 . The oxides Co^2O^3 and Co^2O^{11} appear to be stable at a low red heat. The following hydrates of the former have been prepared: $\text{Co}^2\text{O}^3 + 4\text{H}^2\text{O}$, dried over sulphuric acid; $\text{Co}^2\text{O}^3 + 3\text{H}^2\text{O}$ at 100° ; $\text{Co}^2\text{O}^3 + 2\text{H}^2\text{O}$ at 138° , and probably $\text{Co}^2\text{O}^3 + \text{H}^2\text{O}$ at 300° (Bayley).

A concentrated acid solution of nicotine sulphate, saturated with aluminium hydroxide, deposits octohedral crystals of nicotine-alum (Kirchmann).

Oxidation.—When pure nicotine, boiling at 240° – 242° (uncorr.; thermometer in vapour) is oxidised by potassium permanganate, added as long as it is decolorised, (10 grams nicotine in 500 c.c. of water require about 60 grams of permanganate dissolved in 2000 c.c. of water), it yields carbonate and *pyridine-carboxylate* of potassium. Free pyridine-carboxylic acid, $C^5H^5NO_2$, or $C^5H^4N.COOH$, is obtained by filtering the solution from manganese dioxide, evaporating to dryness, taking up with alcohol, converting the dissolved potassium salt into silver salt, and decomposing it with sulphuretted hydrogen. After crystallisation from hot alcohol or water, it forms colourless crystals, melting at 225° – 227° (uncorr.), and only sparingly soluble in ether and chloroform. This compound unites both with acids and with bases. Its *platinichloride*, $(C^5H^5NO_2)^2 \cdot 2HCl.PtCl^4 + 2H_2O$, forms large well-defined crystals which give off their water at 115° . The *potassium salt*, $C^5H^4N.KNO_2$, is anhydrous; the *calcium salt*, $(C^5H^4NO_2)^2Ca + 5H_2O$, is obtained by slow evaporation of the aqueous solution in large crystals which effloresce slowly at ordinary temperatures, and give off the whole of their water at 115° . The *silver salt* has a constant composition only after recrystallisation from hot water. The salts distilled with lime yield a large quantity of pyridine.

Pyridine-carboxylic acid is identical with the *nicotinic acid* which Huber obtained (vii. 866) by oxidising nicotine with chromic acid mixture (Läublin, *Deut. Chem. Ges. Ber.* x. 2136). Its formation from nicotine shows that this base may be regarded as dipyrindine, $C^{10}H^{10}N^2 + 4$ atoms of hydrogen (Cahours a. Etard).

Action of Sulphur.—When 100 parts of nicotine were heated to 140° with 20 pts. of sulphur, hydrogen sulphide was evolved, and continued to escape as the temperature rose to 155° . At 160° – 170° , the highest temperature attained, the perfectly fluid mass assumed a chrome-green colour; and when left at rest for some days, deposited yellow prismatic crystals, which, after being purified by washing with cold alcohol, and then recrystallised from boiling alcohol, had the composition $C^{20}H^{18}N^4S$. These crystals are of a sulphur-yellow colour, slightly soluble in cold, but readily in hot alcohol, insoluble in water, slightly soluble in benzene, and still less so in ether. They melt at 155° , and on cooling form a resinous yellow mass, which, when subjected to dry distillation, evolves sulphuretted hydrogen, whilst carbon is deposited, and a small quantity of a volatile oil distils over.

The compound $C^{20}H^{18}N^4S$ has a perfectly neutral reaction, but nevertheless forms definite salts with acids. The *hydrochloride*, $C^{20}H^{18}N^4S.2HCl$, crystallises in fine golden yellow needles. The *sulphate* has not yet been obtained in a definite crystalline form. In solutions of the hydrochloride, *platinum tetrachloride* gives an amorphous yellow precipitate of the salt $C^{20}H^{18}N^4S.2HCl.PtCl^4$. *Mercuric chloride* gives a chloromercurate, $C^{20}H^{18}N^4S.HgCl^2$, soluble in hydrochloric acid, and crystallising in yellow needles. *Picric acid* gives a salt soluble in water, and also crystallising in yellow needles. *Auric chloride* gives an amorphous precipitate, soluble in hot water, from which it separates in brilliant scales. Potassium dichromate, ferro-, and ferricyanide, iodide, and cyanide, all give yellow precipitates.

In the formation of this compound, it appears probable that the nicotine is first transformed into *tetrapyrindine*, $C^{20}H^{20}N^4$, by removal of hydrogen: $2(C^{10}H^{10}N^2) + 2S^2 = 4H^2S + C^{20}H^{20}N^4$, and that a substitution of sulphur for hydrogen then takes place according to the equation, $C^{20}H^{20}N^4 + S^2 = H^2S + C^{20}H^{18}N^4S$. The substance is therefore *thiotetrapyrindine*. Its relation to nicotine may be shown by the formula $(C^{10}H^8N^2)^2S$. The action of an excess of sulphur at a higher temperature gives rise to another body not yet isolated (Cahours a. Etard, *Compt. rend.* lxxviii. 99).

NIOBIUM, Nb = 94. Metallic niobium is obtained by passing the vapour of the pentachloride mixed with hydrogen through a red-hot tube. It has a steel-gray colour and splendid metallic lustre; is not attacked at ordinary temperatures by hydrochloric acid, nitric acid, or a mixture of the two, but dissolves quickly in strong sulphuric acid, forming a colourless solution. When heated in a stream of air it burns to the pentoxide, Nb_2O_5 . It does not unite with chlorine at ordinary temperatures, but when heated in the gas it is converted into the pentachloride, together with a small quantity of oxychloride (Roscoe, *Chem. News*, xxxvii. 25).

Niobium trichloride, $NbCl_3$, is obtained by passing the vapour of the pentachloride through a red-hot tube, and is deposited on the sides of the tube in the form of a black crystalline film, having the aspect of iodine. It is neither volatile nor deliquescent, and is not decomposed either by water or by ammonia, but nitric acid converts it into niobic acid.

When the vapour of niobium oxychloride mixed with carbon dioxide is passed over

red-hot charcoal, no decomposition takes place, but if the carbon dioxide be replaced by chlorine, niobium pentachloride is formed. When the trichloride is heated in a stream of carbon dioxide, a white sublimate of niobium oxychloride is produced, together with carbon monoxide. This is the first known instance of the decomposition of carbon dioxide by a metallic chloride (Roscoe).

Carbonitrides.—When a mixture of niobium pentoxide and sodium carbonate, or a niobate containing a little alkali, is heated with charcoal, an olive-coloured crystalline mass is obtained, having, according to the duration of the heating, the composition $\text{NbC}.\frac{2}{3}\text{NbN}$ or $\text{NbC}.\frac{1}{3}\text{NbN}$. If the heat be kept up for six or seven hours at the melting point of nickel, long, highly lustrous, grey-blue needles are obtained, consisting of $\text{NbC}.\frac{1}{3}\text{NbN}$. At intermediate temperatures intermediate products are formed. These several carbonitrides treated with chlorine yield nothing but niobium chloride without a trace of oxychloride, a proof that in their preparation from the pentoxide the whole of the oxygen has been expelled. At the same time there is formed a small quantity of carbon hexchloride, and finely divided charcoal. The carbonitrides heated with copper oxide or lead oxide are completely burned and give off the whole of their nitrogen. When roasted in the air they yield a very bulky pentoxide of niobium. Similar compounds are formed with tantalum (*q. v.*) (A. Joly, *Compt. rend.* lxxxii. 1195).

On the *Ferrocyanides of Niobium*, see CYANIDES (p. 613).

Niobic Oxide, Acid and Salts. The following hydrates and salts are described by B. Santesson (*Bull. Soc. Chim.* [2], xxiv. 52).

The hydrate, $4\text{H}^2\text{O}.3\text{Nb}^2\text{O}^5$, is prepared from the crude hydrate (obtained by fusing niobium pentoxide with potassium bisulphate and treating the melt with water) by dissolving it in hydrochloric acid and precipitating with ammonia. Another hydrate, $7\text{H}^2\text{O}.\text{Nb}^2\text{O}^5$, is prepared by precipitating a boiling solution of sodium niobate with dilute sulphuric acid.

Potassium Niobate (a), $2\text{K}^2\text{O}.4\text{Nb}^2\text{O}^5 + 11\text{H}^2\text{O}$, is obtained by fusing equal parts of niobium pentoxide and potassium carbonate, and treating the fused mass with water, which leaves the niobate insoluble.

(b) $2\text{K}^2\text{O}.\text{Nb}^2\text{O}^5 + 11\text{H}^2\text{O}$, is prepared by fusing the preceding salt with a large excess of potassium carbonate, and subsequent treatment with water.

Sodium Niobate (a), $\text{Na}^2\text{O}.\text{Nb}^2\text{O}^5 + 6\text{H}^2\text{O}$, obtained by boiling niobic acid with sodium hydrate. The residue is separated from the alkaline solution, and dissolved in water. After some time the salt is deposited in small crystals.

(b) $2\text{Na}^2\text{O}.3\text{Nb}^2\text{O}^5 + 9\text{H}^2\text{O}$, obtained by fusing niobium pentoxide with sodium hydrate, and subsequent treatment with boiling water, which leaves the salt insoluble.

Zinc fluoniobate, $\left. \begin{matrix} \text{Zn}^2 \\ \text{H}^2 \end{matrix} \right\} \text{Fl}^{30}\text{Nb}^5 + 28\text{H}^2\text{O}$, obtained by dissolving equivalent quantities of zinc carbonate and niobic acid in concentrated hydrofluoric acid, crystallises, by evaporation, in well-formed prisms, which are insoluble in cold water, decomposed by boiling water, and in the air evolve hydrofluoric acid.

The fluoniobates of cadmium, manganese, cobalt, and nickel are obtained in the same way as the above, and have a corresponding composition.

Iron fluoniobate, $\left. \begin{matrix} \text{Fe}^3 \\ \text{H}^4 \end{matrix} \right\} \text{Fl}^{20}\text{Nb}^5 + 19\text{H}^2\text{O}$, obtained by dissolving equivalent quantities of metallic iron and niobic acid in hydrofluoric acid, crystallises in slender prisms of a yellowish colour.

Copper fluoniobate, $\left. \begin{matrix} \text{Cu}^2 \\ \text{H} \end{matrix} \right\} \text{Fl}^{10}\text{Nb} + 9\text{H}^2\text{O}$, forms broad flat crystals of a bluish colour, which are decomposed by water.

Mercury fluoniobate, $\text{Hg}^2\text{Fl}^{11}\text{Nb} + 8\text{H}^2\text{O}$, is prepared from a solution of equal quantities of mercury oxide and niobic acid in hydrofluoric acid. Mercury fluoride is first deposited, then a white mass, and finally, when the solution is concentrated, the above salt in short prismatic crystals, which are decomposed by water (Santesson).

According to A. Joly, niobic acid forms four series of salts represented by the formulæ



which may be prepared by fusing the pentoxide with a metallic chloride, and keeping the mixture for several hours at a temperature a little below the volatilising point of the chloride. In some cases the chloride was replaced by a mixture of a metallic fluoride with a chloride of alkali-metal.

Magnesium Niobate, $4\text{MgO}.\text{Nb}^2\text{O}^5$, prepared as above, is obtained in large trans-

parent hexagonal plates, with a fatty lustre, like that of mica. Sp. gr. = 4.3. A prismatic niobate, $3\text{MgO} \cdot \text{Nb}_2\text{O}_5$, was prepared in like manner.

Calcium Niobates.—The dicalcic salt, $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$, was obtained by fusing the pentoxide with a large excess of calcium chloride, in the form of very distinct rhomboidal prisms. The monocalcic salt, $\text{CaO} \cdot \text{Nb}_2\text{O}_5$, was obtained by fusing together at a bright red heat for four or five hours, a mixture of niobic acid, calcium fluoride, and potassium chloride, the latter in large excess; but if the fluoride was in excess, the salt, $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$, was formed, together with an oxyfluoride of niobium.

Manganese Niobate.—Manganous fluoride, reacting on niobic acid, gives rise to manganese niobate, which is obtained in transparent, rose-coloured, right rhomboidal prisms. The action of ferrous fluoride does not produce a corresponding salt.

Yttrium Niobate was prepared by fusion, in the form of very small octohedrons, having the composition $\text{Y}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$, which, according to Rammelsberg, corresponds exactly with the formula of native yttrium niobate, *fergusonite*.

The substitution of tantalic acid for niobic acid gave analogous results in almost every instance (see TANTALUM).

Native Niobates.—The following have been examined by J. L. Smith (*Sill. Am. J.* [3], xiii. 361). **Columbite from North Carolina.**—Found in Mitchel Co., and Yancey Co., in rocks belonging to the same epoch as those in which samarskite was discovered. Occurs either in crystals, or in masses weighing from 5 to 100 grams. Sp. gr. of the crystals = 5.562; of the massive variety = 5.485. The following is the analysis of the two forms:—

	Massive	Crystals
Niobic oxide	80.82	80.06
Tungstic and stannic oxides	1.02	1.21
Ferrous oxide	8.73	14.14
Manganous oxide	8.60	5.21
Cupric oxide	trace	—
	99.17	100.62

Columbite from Colorado.—Some crystals of amazon-stone from El Paso Co. were found to have small, black, acicular crystals imbedded beneath the surface. These latter were found to have the specific gravity 5.15. Their composition is as follows:— $\text{Nb}_2\text{O}_5 = 79.61$, $\text{FeO} = 14.14$, $\text{MnO} = 4.61$; loss by heat = 0.5.

Samarskite.—Occurs principally in a mica mine, Mitchel Co., N. Carolina. It is crystalline, black, brittle; fracture conchoidal; lustre vitreous; hardness = 5.5 to 6. Sp. gr. = 5.72. Composition as follows:—

	1	2	3
Niobic oxide	55.13	54.96	37.20
Tantallic oxide	—		
Tungstic and stannic oxides	0.31	0.16	0.08
Yttria	14.49	12.84	14.45
Cerium oxides (?)	4.24	5.17	4.25
Uranium oxide	10.96	9.91	12.46
Manganous oxide	1.53	0.91	0.75
Ferrous oxide	11.74	14.02	10.90
Magnesia	trace	0.52	0.55 CaO
Loss on ignition	0.72	0.66	1.12
Insoluble residue	—	1.25	—
	99.12	100.40	100.36

Finkener a. Stephens (*Verhand. Min. St. Pet.* 1863, 13) found 4 per cent. zirconia and 6 per cent. thorina in this mineral.

Euxenite.—Found associated with samarskite, of a hair-brown colour, giving an ash-coloured powder, translucent in thin splinters. Fracture sub-conchoidal and irregular; lustre resinoid. Sp. gr. (mean) = 4.608. No crystals were found. Analysis gave the following numbers:—

Nb_2O_5	WO_3 and SnO_2	Yttrium and cerium oxides	CaO	UO_3	MnO	FeO	H_2O
54.12	0.21	24.10	5.53	9.53	0.08	0.31	5.70 = 99.58

Fergusonite.—Found in the granite quarries of Rockport, particularly at the intersection of two trap dykes.

The mineral is of a fine, dark brown colour, with a clear conchoidal fracture, and resinous lustre. Hardness 6; sp. gr. 5.681; streak light brown; powder ash-coloured. When heated to bright redness for 15 minutes, it changes to light greenish-

yellow, with loss of 1·5 per cent. $Nb_2O_5 = 48·75$, $Y_2O_3 = 46·01$, $CaO = 4·23$, Fe_2O_3 , and $UO_3 = 0·25$, $H_2O = 1·66$.

Aeschynite and Samarskite (Rammelsberg, *Jahrb. f. Min.* 1878, 529).—

1. *Aeschynite*, sp. gr. 5·16, gave by analysis:—

Nb ² O ⁵	TiO ²	ThO ²	Ce ² O ³ , La ² O ³ , Di ² O ³	Y ² O ³ , Er ² O ³	Fe ² O ³	CaO
32·51	21·20	17·55	19·41	3·10	3·71	2·50 = 99·98

Hence the formula $R^2Nb_2(Ti,Th)^2O^{14}$, or else $R^2Nb_2(Ti,Th)^4O^{20}$.

2. *Samarskite*, (a.) from Miask, sp. gr. = 5·672; (b.) from Mitchell County, North Carolina, sp. gr. = 5·839. In neither case could Rammelsberg detect the presence of acids of zirconium or thorium, which, according to some authorities, exist in this mineral:—

a.	SnO ²	TiO ²	SiO ²	Ta ² O ⁵	Nb ² O ⁵	Y ² O ³	Er ² O ³	Ce ² O ³ (Di)	Fe ² O ³ (Mn)	UO ³
	0·22	1·08	—	—	55·34	8·80	3·82	4·33	14·30	11·94 = 99·83

b.	SnO ²	TiO ²	SiO ²	Ta ² O ⁵	Nb ² O ⁵	Y ² O ³	Er ² O ³	Ce ² O ³ (Di)	Fe ² O ³ (Mn)	UO ³
	0·16	—	0·56	14·36	41·07	6·10	10·80	2·37	14·61	10·90 = 100·93

The mineral therefore consists essentially of a heminiobate (tantarate) isomorphously mixed with a uranate; and as $U : (Nb,Ta) = 1 : 10$ nearly, the formula of samarskite is $\frac{8R^2Nb_6O^{21}}{R^4U_3O^{21}}$ }, or,



Hatchettolite, a new mineral from North Carolina, occurs, associated with euxenite and samarskite, in the combination $O \cdot \infty O \cdot 303$, of yellow-brown colour with greyish shimmer, greenish-yellow after heating. It was regarded by Dana as pyrochlore, but differs from that mineral by containing a larger proportion of uranic oxide.

Rogersite occurs as a deposit, in white botryoidal crusts—evidently a product of decomposition—on euxenite, and more rarely on samarskite. Hardness = 3·5. Analyses 1, 2, 3, Hatchettolite; 4 and 5, Rogersite.

	Nb ² O ⁵	WO ³ and SnO ²	UO ³	CaO	YO	FeO	K ² O	Loss on ignition	Lead	
(1.)	66·01	0·75	15·20	7·72	2·00	2·08	0·50	5·16	trace	= 99·42
(2.)	67·86	0·60	15·63	7·09	0·86	2·51	1·21	4·42	trace	= 100·18
(3.)	67·25	0·91	16·01	7·11	0·64	2·12	—	5·02	trace	= 99·06
								H ² O		
(4.)	18·10	—	—	—	60·12	—	—	17·41		
(5.)	20·21	—	—	—	—	—	—	16·34		

Rogersite is interesting as being the first niobate in which so large a proportion of water has been found (J. L. Smith, *Compt. rend.* lxxxiv. 1036).

An elaborate paper on the metals of the tantalum group has been published by R. Hermann (*J. pr. Chem.* 1877, [2], xv. 105–150; abstr. *Jahresb. f. Chem.* 1877, 288; *Chem. Soc. J.* xxxii. 166), in which—contrary to the view deduced from the experiments of Marignac a. Blomstrand in 1865, and now adopted by all other chemists—he regards these metals as heptads [niobium fluoride, NbF_7 , niobic oxide, Nb_2O_7 , &c.] He further still maintains the separate existence of the metal to which, in 1846, he gave the name ‘ilmenium’ (iii. 244), and is of opinion that the metal which Marignac obtained in 1868 (*Compt. rend.* lvi. 180) by the reduction of the double fluoride, which he supposed to be potassium-niobium fluoride, was really not niobium, but ilmenium.

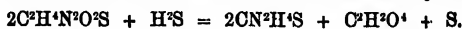
Lastly, Hermann announces the discovery of a new metal of this group, which he names ‘Neptunium.’ Its atomic weight, determined by the analysis of potassium-neptunium fluoride, $4KF \cdot Np^2F^7 + 2H_2O$, he estimates at 118. Neptunium fluoride is described as resembling tantalum fluoride in giving with caustic soda an amorphous precipitate insoluble in boiling water, whereas the fluorides of niobium and ilmenium form with soda-ley crystalline precipitates of sodium salts soluble in 25 pts. of boiling water. From tantalum, neptunium is said to be especially distinguished by the fact that its fluoride forms with potassium fluoride an easily soluble double salt, whereas the fluoride of potassium and tantalum requires 200 pts. of boiling water to dissolve it. A characteristic reaction of neptunium is the wine-yellow colour imparted by neptunic oxide, and the golden-yellow colour by sodium neptunate, to a bead of phosphorus-salt, tantalic oxide giving therewith a colourless, niobic oxide a blue, and ilmenic oxide a brown bead. A further distinction is afforded by the reactions of the

corresponding acids with gallotannic acid, tantalic acid giving a sulphur-yellow, niobic acid an orange, ilmenic acid a brick-red, and neptunic acid a cinnamon-brown precipitate.

NITRACETANILIDE, $C^6H^3.NH.C^2H^2(NO^2)O$. Both this compound and the nitraniline prepared from it (mixture of *o*- and *p*-nitraniline, see p. 198), when boiled with strong soda-ley, are converted, with copious evolution of ammonia, into para-nitrophenol (m. p. 114°), whereas meta-nitraniline prepared from ordinary dinitrobenzene cannot in any way be converted into the corresponding nitrophenol (P. Wagner, *Ber.* vii. 76).

NITRACETHIAMIDE, $C^2H^4N^2O^2S = H^2(NO^2)C.CS.NH^2$ (A. Steiner, *Deut. Chem. Ges. Ber.* viii. 1177; ix. 779). This body is formed, together with ammonium thiocyanate, when dry hydrogen sulphide is passed into anhydrous ether in which mercuric fulminate is suspended. The ether filtered from mercuric sulphide leaves on spontaneous evaporation, nitracethiamide, free sulphur, and an aqueous solution of ammonium thiocyanate and oxalic acid. The nitracethiamide may be separated from the last-mentioned substances by levigation and washing with water, and obtained in the pure state by dissolving it out from the mercuric sulphide with ether.

Nitracethiamide, when examined by the microscope, appears to be made up of prisms. It is quite insoluble in water, moderately soluble in alcohol and ether, and can be separated from these solutions only by spontaneous evaporation of the solvent, since it is decomposed, with separation of sulphur, even below the boiling point of ether. It is quickly decomposed on gentle heating with water, still more quickly with aqueous ammonia, into carbon dioxide and ammonium thiocyanate, with separation of sulphur if the heat be quickly applied. When treated in ethereal solution with hydrogen sulphide, it is resolved into oxalic acid, ammonium thiocyanate, and sulphur:



The product did not appear to contain any amines formed by reduction of the nitro-group. Nitracethiamide, heated with chloride of lime, yields chloropierin.

NITRACETONAPHTHALIDES, $C^{10}H^7.NH.C^2H^2(NO^2)O$. Three isomeric bodies of this composition are formed by the action of nitric acid on acetone-naphthalene dissolved in acetic acid (see NAPHTHALENE). Two of them, α and β , separate from the resulting solution by slow crystallisation, the α -modification in thick prismatic crystals, the β -modification in needles which may be removed by elutriation. Both melt at 171° , and are converted by alcoholic potash into nitro-naphthylamines, by boiling with caustic soda into nitronaphthols. The mother-liquor from which the α - and β -compounds have separated deposits, on addition of water, a third or γ -nitraceto-naphthalide which crystallises in long needles melting at 189° , and reacts like the α - and β -modifications. The following table exhibits a comparative view of the crystalline forms and melting points of these isomeric compounds:

Nitraceto-naphthalide	α Needles	β Prisms	γ Needles
m. p.	171°	171°	189°
Nitronaphthylamine	" 191°	158° – 159°	191°
Nitronaphthol	" 194°	128°	164°
Nitronaphthalene	" 58°	—	58°
Amidonaphthol hydrochloride	" Needles	Scales	Needles
Naphthoquinone	" 125°		125°

(Liebermann a. Dittler, *Ber.* vi. 947; vii. 240); compare p. 1362.

NITRACETONITRIL, $C^2H^2(NO^2)N = CH^2(NO^2).CN$. When finely pulverised ammonium fulminate is gradually treated with five to six times its weight of ordinary sulphuric acid, the mass becomes warm and gives off carbon dioxide, and if it be further heated, and not stirred, nitracetonitril is also given off, and may be condensed in drops which solidify in the crystalline state. It then forms long colourless crystals which melt at a temperature a little above 40° , and dissolve readily in alcohol and in ether. In water, the compound forms heavy oily drops. When heated on platinum-foil, it burns with a very bright flame. If the action of sulphuric acid on ammonium fulminate be moderated by cooling and agitation, and heat applied from time to time only, then, on diluting with a large quantity of water, after the mass has cooled and the evolution of carbon dioxide has ceased, a white crystalline precipitate is formed consisting of an isomeric or polymeric nitracetonitril, and the mother-liquor contains ammonia. This nitracetonitril dissolves in hot water and in strong nitric and sulphuric acids, but is insoluble in cold water, also in ether and in alcohol. It melts, with decomposition, at 216° , and detonates when heated on platinum foil. Its aqueous solution has an acid reaction, and forms, with mercuric nitrate, a white precipitate,

and with silver oxide a white precipitate which soon turns black. The mercury-compound, probably $(C^2HN^2O^2)^2Hg$, is sparingly soluble in hot water, and detonates when heated on platinum foil. Boiling baryta-water decomposes the nitracetonitril, with rapid evolution of ammonia and formation of barium carbonate, the resulting solution containing a crystallisable barium salt. By tin and hydrochloric acid, the nitracetonitril is quickly reduced to a primary amine (Steiner).

NITRACETOPHENONE. See PHENYL-METHYL KETONE.

NITRACETOXYLIDIDE, $C^{10}H^{12}N^2O^2$. See XYLIDINE.

NITRACETYL MESIDENE. See MESITYLENES (AMIDO-), p. 1283.

NITRANIL, $C^6(NO^2)^4O^2$, syn. with TETRANITROQUINONE. See QUINONE.

NITRANILIC ACID, $C^6H^2(NO^2)^2O^4$, syn. with DINITRO-DIOXYQUINONE. See QUINONE.

NITRANILINES. See BENZONES (NITRAMIDO-), p. 198.

NITRIFICATION. The occurrence of nitre in various parts of the earth's surface has been known from the earliest times. It is found in certain cases as an efflorescence on soil, on the sides of caves (generally those frequented by animals), and on old walls, especially those of stables. From this mode of occurrence, the name of 'Saltpetre' is doubtless derived. Large quantities of effloresced nitre are collected in certain districts of North India from the soil surrounding the house drains of the villages (W. J. Palmer, *Chem. Soc. J.* 1868, 318); this nitre, when recrystallised, forms the well-known East Indian saltpetre. Other well-known nitre-yielding districts occur in Algeria (where the mounds covering the sites of ancient villages are lixiviated for nitre), at Saragossa and Murcia in Spain, at Tacunga in Ecuador, and above all on the tableland of Tamaragual in Peru, where an enormous formation of sodium nitrate is found.

Chemical analysis has shown that nitrates are far more widely distributed than would appear from these instances of their marked production; that, in fact, nitrates are generally to be found in all soils and porous rocks on the earth's surface, and especially in fertile well-manured soils. The amount of nitrates present is extremely variable, depending not only on the nature of the soil, but still more on the immediately preceding weather. Nitrates are found in maximum amount after long continued dry weather, when the water of the subsoil has been brought to the surface by capillary attraction, and the salts held in solution have accumulated there as the water evaporates. They are found in minimum quantity after heavy rain, by which they are washed out of the surface soil into the sub-soil, a part being in most cases permanently lost by drainage into rivers, and finally into the sea. The facts relating to the rise and fall of nitrates in a soil are of the greatest importance in practical agriculture, as plants derive their chief supply of nitrogen from the nitrates which the soil contains. A soil, or porous rock, may be very rich in nitrates without yielding the efflorescence characteristic of nitre-bearing strata; an efflorescence generally occurs only when the nitric acid is combined with potassium; the nitrate most commonly present in soil is nitrate of calcium, and this is too deliquescent in its nature to appear as a dry salt, even under favourable conditions of climate.

The conditions under which nitrates may be formed in soil have been long known. The necessity of obtaining nitre for the manufacture of gunpowder led to an early attention being given to the subject, and in most countries of continental Europe the artificial production of nitre has been conducted on a large scale, and brought to considerable perfection. This manufacture is now superseded by the production of nitre by means of the reaction between Peruvian nitrate of sodium and chloride of potassium.

The earliest manufacture of nitre was simply by the lixiviation of old plaster, and of the earthen floors of stables, cottages, &c., wood ashes being added to convert the nitrate of calcium into nitrate of potassium. The actual production of nitre seems to have been first successfully accomplished by Glauber in the seventeenth century. Numerous investigations on the subject were made during the next century in Sweden, Germany, and France, the work being stimulated by the offer of large prizes by the respective governments for the best method of producing saltpetre. The various methods thus brought into use were quite similar in principle; they all aimed at accomplishing in a more rapid manner, and on an exaggerated scale, the process by which nitre is naturally produced in soil.

The materials used for constructing an artificial nitre bed consisted, in the first place, of a rich porous soil, that remaining from the lixiviation of a former bed being far superior to any other. To this soil were added limited quantities of farmyard manure, various kinds of animal and vegetable refuse, and wood ashes or calcareous

matter; straw was added, if required, to keep the mass porous, and the whole was watered with urine. In this first stage of the process no nitre is formed, putrefactive change being inimical to the production of nitrates; the object in view is simply to obtain a soil extremely rich in nitrogenous humic matter.

Such a soil having been prepared, it is, on the French plan, formed into a long mound under a shed erected for the purpose. If the mound of soil is very large, aëration may be provided for by tunnels of open woodwork penetrating the mass at regular intervals; with smaller heaps it is sufficient to stir the earth from time to time with a rake, or turn it with a spade. The watering of the earth is a matter requiring great judgment, a certain degree of moisture being most suitable for nitrification; with an excess of water nitrification will cease altogether, while if the soil is too dry the nitrification proceeds but slowly. Urine may be used at first for watering the mass, but as the operation advances water only must be employed, and in diminishing quantity. At the end of two years from the formation of the mound the soil will be ready for extraction: 1000 lbs. of the nitrified soil may be expected to yield 5 lbs. of crude nitre.

On the German plan the prepared soil is built into thick walls, 6 or 7 feet high; one side of the wall is plane, the other is disposed in gutter-shaped terraces; each wall is roofed with straw. A series of these walls is arranged on an impervious terrace, freely exposed to the weather. The earth is watered when necessary on the terraced side of the wall; any drainage which may occur during heavy rain is collected, and applied to the earth in dry weather. As the earth becomes rich in nitre this salt tends to effloresce on the plane side of the wall; this side is then from time to time scraped off, the earth thus removed is lixiviated, and returned with fresh soil to the terraced side of the wall. The production of nitre on this plan proceeds with tolerable regularity, and the walls gradually march across the terrace.

The experience thus gained by practice revealed many of the conditions necessary for the production of nitrates in soil. For a soil to nitrify it must have—1. Free access of air; 2. A suitable amount of moisture; 3. A suitable temperature (10° – 25° according to Dumas); 4. The presence of a salifiable base, with which the nitric acid might combine; 5. The presence of nitrogenous organic matter, which must however have passed the first putrefactive stage of decomposition. To these conditions we might perhaps add—6. Darkness,—light being necessarily excluded from the interior of a mass of soil.

We must now turn to the various theories by which the process of nitrification has been explained.

As nitre is continually found as an efflorescence upon the surface of the nitrifying matrix, it was assumed by the alchemists that nitre was of aerial origin, and this theory has been more or less held down to the present day. J. Davy, as the result of his examination of the nitre caverns in Ceylon, concluded that the nitric acid was formed from the nitrogen and oxygen of the air. Longchamp fully enunciated this theory. He regarded the combination of the atmospheric nitrogen and oxygen dissolved in the water of moist porous bodies as the only source of nitric acid. De Saussure and Proust also held that the nitrogen of the air is oxidised to nitric acid during nitrification. Clôez, in his excellent lecture on nitrification (*Leçons de Chimie et de Physique professées en 1861 à la Société chimique de Paris*), considers that such a combination of nitrogen and oxygen is induced by the presence of other matter undergoing oxidation, and believes that this oxidation of the nitrogen of the atmosphere is one of the sources of nitric acid in the nitrification of soil.

A very similar theory has been held by many chemists to explain the nitrification of organic matter. The organic matter during its decomposition is considered to evolve nitrogen, and this in its 'nascent' state is oxidised by the oxygen of the air, which may be present in a condensed form on the surface of porous bodies. This explanation is the one given by Hofmann (*Exhibition Report*, 1862, 47).

The above theories have also been modified by the substitution of ozone for oxygen. According to Schönbein free nitrogen can be oxidised by ozone into nitric acid. The same view has been held quite recently by S. W. Johnson. Ozone is assumed to be formed during the oxidation of the organic matter of the soil, this ozone then attacking the free nitrogen present and producing nitric acid.

The truth or fallacy of the theories of nitrification we have just sketched is of the greatest importance to practical agriculture, for if the nitrogen of the air can be oxidised to nitric acid in the soil, it is clear that we have in nitrification an actual creation of plant-food. The weight of evidence is however apparently against the views just noticed. Nitrogen and oxygen certainly combine at a very high temperature, as that given by the electric spark (Cavendish), or produced by heating platinum to its melting point (H. Davy), or by the combustion of hydrogen in oxygen; but at somewhat lower temperatures, as that of hydrogen burning in air, no nitrous or nitric

acid is produced if the materials used are perfectly free from ammonia (L. T. Wright, *Chem. Soc. J.* 1879, xxxv. 42). Porous bodies also appear to be without effect in inducing the combination of nitrogen and oxygen. Neither charcoal (L. H. Wood) nor spongy platinum (Kuhlmann) is capable of bringing about the combination of oxygen and nitrogen, even at a high temperature. Ozone also appears incapable of oxidising nitrogen. Lawes, Gilbert and Pugh found that no nitric acid was produced by passing ozonised air for several months over alkaline pumice. Carius has also recently shown that ozone is without effect on gaseous nitrogen. A further proof that the nitrogen of the atmosphere takes no part in the process of nitrification is afforded by one of the experiments of Boussingault (*Compt. rend.* lxxvi. 22). He determined the total amount of nitrogen in a soil rich in humic matter, and then placed two weighed quantities of this soil, one mixed with a small quantity of cellulose, in large glass vessels containing an abundant excess of air; the vessels were then closed and kept in a cellar for eleven years. At the end of this time the contents of the vessels were analysed. The soils had in each case formed a large amount of nitric acid, but the total nitrogen, determined by combustion with oxide of copper, was found to have somewhat diminished; the nitrogen of the air had thus not entered into combination.

The second group of theories we have to notice regards the oxidation of ammonia as the source of the nitric acid formed in soil. This view was partly held by several of the older chemists, but was first strongly insisted upon by Kuhlmann. He proved by many experiments with powerful oxidising agents that ammonia might readily be converted into nitric acid, and concluded that by the action of the porous bodies contained in the soil the oxidation of ammonia might be effected and nitric acid produced. This simple explanation of the phenomenon has been held by some down to the present day. Thus Dehérain (*Wurtz, Dict. Chim.* ii. 564) regards the formation of nitre in the walls of stables as due to the simple oxidation of the ammonia vapours in the porous brickwork. This theory has also been modified by assuming that the oxidation is induced by the disposing influence of other oxidising actions, and by the substitution of the action of ozone for that of the oxygen of the air. A further modification of the above theory regards ferric oxide as the agent for the conversion of ammonia into nitric acid. The latter view has been held by P. Thenard, Knop, Haarstick, and Pesci. On the whole, the explanation of nitrification as due to the oxidation of ammonia has been perhaps the opinion most generally held by modern chemists.

Respecting this group of theories it will suffice to state that the oxidation of ammonia by ozone has apparently been established by Banmert, Houzeau, and Carius (*Liebig's Annalen*, clxxiv. 31), but that there is very little evidence of the production of nitric acid from ammonia by the action of the oxygen of the air at ordinary temperatures. The power of ferric oxide to convert ammonia into nitric acid is denied by Millon and Storer.

Though, however, the oxidation of ammonia has not been satisfactorily accomplished in the laboratory, save by means of powerful reagents, or at high temperatures, there is no doubt that ammonia is rapidly oxidised in a fertile soil, and that this oxidation of ammonia is a considerable cause of the production of nitric acid. An excellent illustration of the oxidation of ammonium salts by soil is afforded by the analyses of the drainage waters from the experimental wheat field at Rothamsted. The following table shows the composition of the drainage water running from the plots of this field immediately before and immediately after the application of ammonium salts. The ammonium salts were applied between March 10 and 13, 1879.

Nitrogen, existing as Nitrates, per million of Drainage water.

Date of running	Plots with no ammonia				Plots receiving 400 lbs. ammonium salts per acre							
	3 & 4	5	16	17	7	10	11	12	13	14	18	
February 16 . . .	3.4	3.7	4.2	3.3	3.5	5.2	4.8	4.1	3.8	4.8	4.2	
April 7	3.6	2.9	3.6	2.3	39.0	45.4	41.8	25.4	29.4	33.0	40.4	

On February 16 the proportion of nitric acid in the drain-water is uniformly low throughout the plots. At the next running of the drains the plots which had received no ammonium salts have somewhat diminished their yield of nitrates, while in the case of those plots receiving ammonium salts in the interval the proportion of nitrates in the drainage water has enormously increased. This loss of nitrates by

drainage is a serious cause of diminished fertility to the soil. Further striking illustrations of the oxidation of ammonia by soil will be found in Frankland's experiments on the intermittent filtration of sewage (*Rivers' Pollution Commission, 1868, First Report, p. 60*).

Besides the oxidation of free nitrogen and of ammonia, it has naturally been assumed that the oxidation of nitrogenous organic matter is a further source of nitric acid. The organic matter has been supposed either to yield in the first place nascent nitrogen or ammonia, and these to be subsequently oxidised, or the organic nitrogen has been regarded as directly converted into nitric acid. The production of nitrates by the action of alkaline permanganate of potassium on nitrogenous bodies has been held to support the latter view. That nitrogenous organic matter does contribute to the formation of nitrates in soil there can be no doubt. In some of Boussingault's experiments (*Compt. rend. lxxxii. 477*) 50 per cent. of the nitrogen of rape cake, and 90 per cent. of the nitrogen supplied as horn filings, were converted into nitric acid after mixture with soil.

The theories explanatory of nitrification just reviewed have satisfied many chemists. Clöez, writing in 1861, says: 'The question of nitrification appears to me to be at present completely elucidated.' The facts however would be more truly stated by saying that chemists had entirely failed, when working with pure substances in the laboratory, to produce nitric acid under the conditions known to occur in soils. Boussingault truthfully sums up his own work by saying 'It is remarkable that in a very large number of experiments made with the view of nitrifying nitrogenous substances, I have never been able to discover the least production of nitric acid in the absence of vegetable earth.'

We turn now to the latest theory of nitrification, which holds that the oxidation of ammonia and of organic nitrogen in the soil is the work of a living organism.

The first suggestion of the possibility of such an explanation was made by Pasteur in 1862. The oxidation of alcohol to acetic acid by the agency of mycoderms appeared to him sufficiently analogous to the phenomena of nitrification to call for a fresh study of the subject from this point of view. An opinion of the same character was expressed by A. Müller in 1873. He observed that the ammonia of sewage, and of certain impure well waters, often changed spontaneously into nitric acid, while similar solutions of pure ammonium salts and urea remained unchanged; he suggested that the first-named liquids probably contained a ferment which was absent from the pure solutions prepared in the laboratory.

To Schloesing and Müntz belongs the credit of establishing this hypothesis by experiment; their first paper on the subject (*Compt. rend. lxxxiv. 301*) was published early in 1877. They found that sewage might be slowly filtered through a porous column of pure sand and limestone without nitrification at first taking place; after twenty days nitrification set in, and the ammonia of the sewage was after this time entirely converted into nitric acid. On allowing chloroform vapour to pour on the surface of the column of sand and limestone, nitrification was wholly suspended, and did not recommence during seven weeks after the chloroform had ceased to be applied. The surface of the column was then seeded by the addition of a little vegetable earth known to nitrify with ease; the result was that nitrification of the sewage at once recommenced as strongly as before. The evidence is here of two kinds—first, the oxidation of the ammonia was entirely prevented by chloroform, which, as Müntz had previously shown, suspends the action of all organised ferments—second, the oxidation of the ammonia was induced by adding to the porous column a few particles of vegetable soil. In a second paper (*Compt. rend. lxxxv. 1018*), Schloesing and Müntz show that heating soil to 100° destroys its capacity for nitrification. If soil is heated to 100°, or treated with chloroform, and then exposed to pure air in a moist state, carbonic acid and ammonia are produced, but no nitrates. Nitrification can however be again started by the addition of a little unheated earth. A porous medium is also not necessary for nitrification; sewage, or a weak solution containing ammonium salts, sugar, and cinereal matter, may be nitrified by passing over polished pebbles, if a little vegetable earth be added as seed.

Between the publication of the two papers just mentioned the investigation of the subject was commenced at Rothamsted (*Chem. Soc. J. 1878, xxxiii. 44*); the results were entirely confirmatory of the ferment theory of nitrification. Moist garden soil contained in glass tubes was exposed to a current of washed air for several weeks, the air in some cases bearing the vapour of chloroform, bisulphide of carbon, or carbolic acid. With washed air alone the proportion of nitrates in the soil increased to five or six times its original amount, while where chloroform or bisulphide of carbon vapour was introduced no nitrification took place; the carbolic acid also hindered nitrification, but being retained by the upper portion of the moist soil its action was less considerable. A further set of experiments was made with a weak solution of chloride

of ammonium, containing about 80 mg. per litre, with small quantities of tartrate and phosphate of potassium, and some precipitated carbonate of calcium. Two bottles of this solution were placed in a window, and two in a dark cupboard, one of each set being seeded by the addition of a little pasture soil. After three months it was found that the unseeded solutions remained unchanged, the seeded solution in darkness had completely nitrified, while the corresponding solution in daylight contained no nitric acid. The conclusions of Schloesing and Müntz were thus entirely confirmed, and the additional fact made known that light is inimical to the work of the nitrifying organism.

This previously unsuspected action of a living organism throws great light on many of the earlier attempts to produce nitrification; former experiments resulting in the production of nitric acid are now clearly valueless as proof of the inorganic character of nitrification, unless the conditions of the experiment were such as to preclude the existence of living organisms.

The evidence on which nitrification in soil and waters is attributed to the action of an organised ferment has been fully stated, the subsequent results obtained by Schloesing and Müntz (*Compt. rend.* lxxxvi. 892; lxxxix. 891, 1074) and at Rothamsted (*Trans. Chem. Soc.* 1879, 429) may be more briefly noticed; the subject is still but incompletely investigated.

The precise nature of the ferment has been sought for by the French experimenters; they found that *Penicillium glaucum*, *Aspergillus niger*, *Mucor mucedo* and *racemosus*, and *Mycoderma vini* and *aceti* are all incapable of producing nitric acid. The results obtained at Rothamsted also show that the ordinary forms of *Bacteria* contained in the atmosphere are also incapable of effecting nitrification.

Schloesing and Müntz in one of their later communications describe the organism which acts as the nitrifying ferment. They obtained it in a pure condition by systematic cultivation. In the first place a sterilised solution (consisting either of sewage, or of artificial mixtures containing ammonium salts with organic and cinereal matter) was seeded by the addition of a few particles of vegetable earth. When nitrification was accomplished a fresh solution was seeded from that just nitrified. By proceeding thus a number of times the nitrifying organism was separated from the numerous other organisms contained in soil.

The organism thus isolated consists of extremely minute, round, or slightly elongated corpuscles, existing either singly or joined in couples; it is of slow growth, and multiplies apparently by budding. It thus apparently belongs to the great bacteria family, the different members of which effect, as is well known, such powerful and divers changes in organic matter. In Cohn's classification it would probably be described as a *Micrococcus*. The nitrifying organism is not easily distinguishable from other organisms of the same class.

The nitrifying bacterium is abundant in soils; it is rare to find a particle of arable soil which is not effective as seed. It is also found abundantly in sewage, but only to a small extent in running water; in the latter it is found attached to the surfaces of solid bodies, and collects at the bottom of the vessel when the water is allowed to stand. Air and rain are apparently, as a rule, free from this organism.

One of the characteristics of the nitrifying organism is the comparative ease with which it may be destroyed by heat; Schloesing a. Müntz found exposure to 90° sufficient for this purpose. Desiccation, according to the French experimenters, also destroys the organism, even when the drying is conducted at ordinary temperatures; soil may thus lose all power of nitrification by drying at the temperature of the air. Long deprivation of oxygen is also fatal. In mediums rich in organic matter *mucor* is the chief enemy to nitrification, and until this fungus has run its course, no nitrification will occur.

The investigations at Rothamsted on the conditions under which nitrification occurs were made with solutions of ammonium chloride, containing phosphates, and generally potassium tartrate; the solutions were placed in wide-mouthed pint bottles filled to the shoulder, giving thus at starting a depth of about 5 inches of fluid; the solutions were seeded with a small quantity of a solution already nitrified, and generally placed in the dark. The conclusions arrived at were as follows.

A solution of suitable composition will not nitrify when seeded if no salifiable base be present. A trace of nitrous acid may be formed, but the action soon comes to an end. If a salt of an organic acid is present, as, for example, a tartrate, nitrification will proceed slowly in proportion as the organic acid is consumed by the organisms present and the base set free. Active nitrification was obtained only in presence of calcium carbonate. The nitric fermentation is in this respect analogous to the lactic and butyric. Alkali carbonates, including carbonate of ammonium, are, according to Schloesing a. Müntz, equally capable of assisting nitrification, but if they amount to more than two or three thousandths of the solution, they retard or com-

pletely arrest the action. Boussingault, in his experiments with soil, did not find that the addition of lime increased the rate of nitrification; the soils he employed were, however, never quite free from lime, and the quantity artificially added possibly produced an excessive alkaline condition.

The presence of organic carbon should be essential for nitrification if this process is really a function of the growth of an organism of low character. Besides the humic matter of soil, tartaric acid and sugar have been found effective as organic food; alcohol, glycerin, and albumin were also found suitable by the French experimenters. The minimum proportion of organic carbon required has not yet been ascertained, but 3 pts. of carbon present as tartrate have proved sufficient for the nitrification of 10 pts. of nitrogen present as chloride of ammonium.

Light certainly hinders nitrification; in many experiments light has stopped the action altogether, and in others retarded it. The nitrifying organism is not apparently killed by exposure to light.

The addition of a small quantity of seed to a suitable solution is not immediately followed by nitrification; a period of inaction follows, which is shorter at high temperatures than at low ones. Thus in the case of 400 c.c. of an 80 mg. per litre chloride of ammonium solution, seeded with 1 c.c. of a solution already nitrified, nitrification commenced in about thirty-eight days at 7°, and in about ten days at 30°. An increase in the concentration of the solution considerably lengthens the period of inaction; in a solution of about eight times the unit strength, the preliminary period of rest was about doubled.

The limits of temperature within which nitrification will take place are, as at present ascertained, as follows. At Rothamsted a purely nitrous fermentation has proceeded with some briskness in very weak solutions at 3°, while a nitric fermentation in a similar solution almost ceased at 5°. Below 5° Schloesing a. Müntz found nitrification to be excessively feeble; at 12° they state it begins to be active. Activity rapidly increases with a further rise of temperature, reaching a maximum at 37°, at which point nitrification is ten times more rapid than at 14°. Above 37° the rate of action rapidly diminishes, and at 45° nitrates are formed less rapidly than at 15°. At 50° very little nitrate is produced, and beyond 55° there is absolutely no action. These determinations of Schloesing a. Müntz differ from the results obtained at Rothamsted, where no nitrification was obtained at 40°, though the solutions were kept fifty-four days at this temperature and twice seeded. The experiments of Schloesing a. Müntz were apparently made with thin layers of solution, exposing a large surface to the air; at Rothamsted the solutions had a considerable depth and small surface; it seems possible that the supply of oxygen was in the latter case insufficient for the requirements of a high temperature.

In experiments made at various temperatures at Rothamsted, the rate of nitrification did not increase so rapidly with the rise in temperature as found by the French investigators. Thus with an 80 mg. solution of ammonium chloride, nitrification occupied about thirty-seven days at 11°, and about eight days at 30°. At a fixed temperature the length of time required for complete nitrification appears to vary almost directly with the degree of concentration of the solution.

The rate of nitrification is not uniform throughout its course; it appears to commence slowly, gradually attains a maximum of energy, and then becomes slow again towards the conclusion of the action.

The product of nitrification is not uniform, sometimes nitrous, and sometimes nitric acid being produced. Nitrites are produced rarely in soil but frequently in liquids; according to the French observers, their occurrence is determined by an insufficient degree of aëration, or by the temperature being too low. They state that a thin layer of liquid (1 or 2 mm.), will yield nitrates, and a thicker layer nitrites. The experience at Rothamsted has been of a different kind; a purely nitric fermentation has been obtained only in the case of weak solutions nitrified at low temperatures; in the case of strong solutions or high temperatures, nitrous acid was chiefly, if not entirely, produced, and was afterwards converted into nitric acid at the end of the reaction. In some cases, however, depending on the character of the ferment used, the result of the action has been merely nitrous acid, even in the case of cold dilute solutions; and in these cases the nitrous acid is permanent, and is not afterwards changed into nitric. The original ferment obtained from pasture soil yields a purely nitric fermentation under suitable conditions; but when nitrified solutions which have been long kept are employed as seed, the phenomena just mentioned may occur. Thus it is quite possible to seed two precisely similar solutions with two samples of ferment, and place the solutions under the same conditions as to temperature and aëration, and to obtain in one case a purely nitric, and in the other a purely nitrous fermentation. The altered ferment is capable of converting ammonia into nitrous acid, but not of converting nitrites into nitrates.

Actual experiments with a solution of potassium nitrite have shown it to be very permanent in the absence of a ferment, to be unaffected by the altered ferment just mentioned, but to be rapidly converted into nitrate by the addition of a few drops of a solution in which nitrites have lately changed into nitrates. The conversion of potassium nitrite into nitrate took place only in the dark.

The whole of the ammonia present in a solution has not been obtained as nitric acid, a small part of the nitrogen passing into organic combinations, or being otherwise lost. On an average of ten experiments, under different conditions of temperature, the nitrogen obtained as nitric acid was 93·7 per cent. of that taken as ammonia, but this result is probably somewhat too low.

Besides the papers already referred to, two papers by Schloesing (*Compt. rend.* lxxvii. 203, 353), treating of nitrification in soil with a limited supply of oxygen, and of the destruction of existing nitrates when oxygen is withheld, may be consulted with advantage.

R. W.

NITRILS, $R-C\equiv N$. *Normal Alcoholic Cyanides*.—These compounds are easily and completely converted into compound others by the action of gaseous hydrogen chloride on their solutions in absolute alcohol; still more readily by the action of sulphuric acid. In this manner the ethylic ethers of acetic, propionic, and benzoic acids are readily obtained (Beckurts a. Otto, *Ber.* ix. 1590).

Preparation of Aromatic Nitrils.—Experiments by K. Schelnberg (*Ber.* x. 746) on the preparation of these bodies have led to the following conclusions: (1). The haloïd compounds of aromatic hydrocarbons react directly with metallic cyanides. (2). Nitrils may be prepared from hydrocarbons and cyanogen gas by direct substitution. (3). Nitrils cannot be prepared from hydrocarbons and the cyanides of the halogen-elements, the reaction yielding nothing but haloïd compounds of the hydrocarbons and hydrogen cyanide.

The experiments were made by passing the vapours of the haloïd compounds in a slow stream over finely pulverised anhydrous *ferrocyanide of potassium*, mixed with a quantity of sand sufficient to prevent melting down, and heated to moderate redness. In this manner, *chloro-* and *bromo-benzene* yielded benzonitril, $C_6H_5.CN$ (at a higher temperature, however; and especially when a gun-barrel was used instead of a glass tube, ammonium cyanide and benzene were formed, with separation of carbon); *di-bromobenzene* yielded a small quantity of benzonitril, together with the nitril of terephthalic acid. A mixture of *ortho-* and *para-chloro-toluene* yielded the corresponding nitrils, convertible into *o-* and *p-toluic* acid; and *bromonaphthalene* at a high temperature yielded α -naphthyl cyanide. It was only in this last case that the yield of nitril was satisfactory; the smallest quantity was obtained in the case of the toluene compounds.

Aromatic nitrils were also produced by heating the corresponding halogen-compounds with excess of metallic cyanide, to 300°–400° in sealed glass tubes, small quantities of ammonia and hydrocyanic acid being also generally formed as secondary products, and in many cases cyanogen gas. Under these circumstances, *potassium ferrocyanide* acts but slowly on *chloro-* or *bromo-benzene*, only 20–22 per cent. of the theoretical amount of benzonitril being obtained after ten hours' heating. Crystallised *bromotoluene* is but very slowly attacked by potassium ferrocyanide; *bromobenzene* and *potassium cyanide* yield a smaller amount of nitril than bromobenzene and the ferrocyanide; *chlorobenzene* and *cyanide of lead* yielded only a small quantity of benzonitril (6·5 per cent. of the theoretical amount), a similar amount was obtained with lead cyanide and *bromo-benzene*, and still smaller amounts by the action of lead cyanide on *parabromotoluene* and *bromonaphthalene*. *Silver cyanide* (mixed with common salt to facilitate its pulverisation) acts on the halogen-compounds above mentioned in the same manner as lead cyanide. *Iodobenzene* and silver cyanide, heated together for ten hours, yielded a quantity of benzonitril from which 26·8 per cent. of the theoretical amount of benzoic acid was obtained; *paraiodotoluene* is less easily attacked; *orthoiodotoluene* behaves like iodobenzene. *Iodonaphthalene* (prepared by the action of iodine dissolved in carbon sulphide on mercury-dinaphthyl) yielded with silver cyanide at 350° large quantities of α -naphthonitril. *Benzene*, *toluene*, and *naphthalene*, heated with mercuric cyanide to 300°–400°, yielded small quantities of the corresponding nitrils.

Benzene-vapour, mixed with excess of cyanogen gas and slowly passed through a red-hot tube filled with fragments of pumice, yielded, with prussic acid, large quantities of benzonitril and small quantities of terephthalonitril; a small quantity of diphenyl, and apparently also of metadiacyanobenzene, was formed at the same time (Schelnberg). *Naphthalene* similarly treated yielded large quantities of α -cyanonaphthalene; the α -naphthoic acid prepared therefrom melted at 160°. *Benzene* and *cyanogen*

bromide, heated together for five or six hours to 220° – 240° , are converted partly into hydrogen cyanide and bromobenzene, partly into unctuous masses; *naphthalene* and *cyanogen bromide* yield in like manner bromonaphthalene, boiling at 276° . *Dimethylaniline* and *cyanogen iodide* act on one another at ordinary temperatures with evolution of heat, forming hydrocyanic acid and monoiododimethylaniline, melting at 79° .

Reaction of Nitrils with Aldehydes.—When *benzonitril* is added, with agitation, to strong sulphuric acid containing 1–1½ per cent. paraldehyde, ethylidene-dibenzamide, $\text{CH}^3\text{.CH}(\text{NHCO}^6\text{H}^3)^2$, is produced; and in like manner benzonitril and *chloral* yield trichlorethylidenedibenzamide, $\text{CCl}^3\text{.CH}(\text{NHCO}^6\text{H}^3)^2$. When benzonitril (2 mols.) is diluted with an equal volume of *chloroform*, the mixture treated with strong sulphuric acid, and *methylal* (1 mol.) added, methylene-dibenzamide, $\text{CH}^2(\text{NHCO}^6\text{H}^3)^2$, is produced (Hepp a. Spiess, pp. 758, 1313).

Methylenediphenylacetamide, $\text{CH}^2(\text{NH.CO.CH}^3\text{.C}^6\text{H}^5)^2$, is obtained by heating 1 mol. methylal and 2 mols. α -tolunitril or benzyl cyanide, $\text{C}^6\text{H}^5\text{.CH}^2\text{.CN}$, first with a mixture of equal volumes of glacial acetic acid and strong sulphuric acid, afterwards with sulphuric acid alone, and pouring the product into water. It forms small needles which melt at 205° , distils almost without decomposition, is nearly insoluble in water, dissolves very sparingly in ether and in ligroin, more readily in carbon sulphide, somewhat abundantly in boiling alcohol and glacial acetic acid. By heating with hydrochloric acid or alcoholic potash, it is converted into phenylacetic acid; with dilute sulphuric acid and manganese dioxide into phenylacetamide (Hepp, *Ber. x.* 1649).

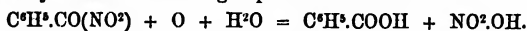
Trichlorethylidene-diphenylacetamide, $\text{CCl}^3\text{.CH}(\text{NH.CO.CH}^3\text{.C}^6\text{H}^5)^2$, obtained by similar treatment from benzyl cyanide and chloral, forms small white needles, which sublime before melting, and are as soluble as the preceding compound in the liquids above mentioned. In like manner are prepared trichlorethylidenediacetamide from chloral and acetunitril, and trichlorethylidene-dibenzamide from chloral and benzonitril (p. 758, Hepp a. Spiess).

NITROBENZILE, $\text{C}^6\text{H}^5(\text{NO}^2)\text{O}^2$. This compound, treated with tin or zinc and hydrochloric or acetic acid, is reduced to amidobenzile, $\text{C}^6\text{H}^5(\text{NH}^2)\text{O}^2$, which crystallises in needles, melts at 94° , and dissolves in 300 pts. of boiling water, very easily in alcohol. The sulphate and oxalate are sparingly soluble and crystallise in needles; the hydrochloride, which is the most soluble of the salts, crystallises in rhombic laminae having a silvery lustre. The platinochloride is unstable.

NITROBENZONAPHTHYLAMIDE. See NAPHTHYLAMINES.

NITROBENZONITRIL. See BENZONITRIL (p. 306).

NITROBENZOYL, $\text{C}^6\text{H}^5(\text{NO}^2)\text{O}$. This name is given by Lippmann a. Hawliczek (*Deut. Chem. Ges. Ber. ix.* 146) to a substance having the composition of nitrobenzoic aldehyde, and occurring in the oil which is formed, together with solid metanitrobenzoic aldehyde (p. 303), by the action of a mixture of nitric and sulphuric acids on bitter almond oil. It is converted by oxidation into benzoic and nitric acids, and therefore probably contains the nitro-group in the side chain:



In accordance with this view of its constitution, it does not exhibit the characters of an aldehyde, and may be separated from admixed bitter almond oil by means of sodium sulphite. It is decomposed by distillation, even under a pressure of 6 lines.

NITROBROMACETANILIDES. See BROMANILINES, under PHENYLAMINES.

NITROBROMANILINES. See BENZENES (NITROBROMAMIDO-), p. 199.

NITROBUTANE. See NITROPARAFFINS, under PARAFFINS.

NITROCARBOL, syn. with NITROMETHANE. See PARAFFINS.

NITROCOLOPHTHALIN. See COLOPHTHALIN, under RESINS.

NITROCRESOLSULPHONIC ACID, $\text{C}^6\text{H}^2(\text{NO}^2)(\text{CH}^3)(\text{OH})\text{.SO}^3\text{H}$. See CRESOLSULPHONIC ACIDS (p. 583). An acid of this composition is formed, with evolution of nitrogen, by the action of a gentle heat on nitrodiazotoluenesulphonic acid. (See TOLUENESULPHONIC ACIDS.)

NITROETHANE. See PARAFFINS.

NITROGEN. On the Quantivalence of this Element, see AMMONIUM SALTS (p. 74).

Occurrence.—From H. Draper's observations on the solar spectrum (*Sill. Am. J.* [3], xiv. 89), it appears probable that nitrogen exists in the sun.

On the occurrence of Nitrogen in Volcanic Gases, see VOLCANOS.

Preparation.—In the preparation of nitrogen by the usual method from ammonium nitrite (iv. 63), W. Gibbs (*Deut. Chem. Ges. Ber.* x. 1387) recommends that the solution of sodium nitrite and ammonium sulphate be mixed with a strong solution of potassium dichromate and heated; the nitrogen is then given off with effervescence and quite free from oxygen-compounds.

On the effect of the *Silent Electric Discharge* on Nitrogen in presence of Water-vapour, see ELECTRICITY (p. 727); also on the oxides N_2O and NO (p. 728).

On the *Refractive and Dispersive Power* of Nitrogen and its Oxides, see LIGHT (p. 1183). On the *Spectrum* of Nitrogen, see SPECTRAL ANALYSIS.

On the *Friction-coefficient* of Nitrogen and its Oxides, see GASES (p. 851; compressibility, p. 853).

The *Expansion-coefficient* of Nitrogen, according to the experiments of Ph. Jolly (*Pogg. Ann.* 1874, *Jubelbd.* 82) is 0.0036677.

On the *Liquefaction* of Nitrogen, see GASES (p. 857).

Absorption.—Experiments on the absorption of nitrogen by the black decomposition-products of carbohydrates have been made by D  h  rain (*Compt. rend.* lxxvi. 1390). The substances experimented on were mixtures of glucose and ammonia, glucose and caustic soda, moist sawdust mixed with limo, old vegetable soil, &c. A mixture of 10 grms. glucose and 40 g. caustic soda absorbed from the air 0.115 g. nitrogen, and from a stream of pure nitrogen 0.072 grm. In these experiments, the oxygen of the air was found to be converted into carbon dioxide, but the nitrogen had entered into combination in such a manner that the substances afterwards gave off ammonia when heated with soda-lime. This absorption of nitrogen takes place even at ordinary temperatures, and is probably of some importance in the nutrition of plants.

According to A. Pagel (*Dingl. pol. J.* ccxxv. 308) humus-substances do not absorb nitrogen from the air. Berthelot finds that under the prolonged influence of feeble electric tensions, such as may be produced by a voltaic battery with its poles unconnected, certain non-nitrogenous organic bodies are capable of absorbing nitrogen; and he thence infers as probable that the tissues and organs of plants under the influence of atmospheric electricity may take up nitrogen from the air and assimilate it as nutriment (*Compt. rend.* lxxxv. 173). See also ELECTRICITY (p. 728).

On the *Absorption of Nitrogen by Iron*, see p. 1113.

Oxidation.—On the direct oxidation of nitrogen to *nitrous* and *nitric acids*, see Berthelot (*Compt. rend.* lxxxiv. 61).

On the *Heat of Oxidation of Nitrogen*, see HEAT (p. 952).

Estimation of Nitrogen in Organic Compounds.—Considerable discussion has taken place respecting the relative accuracy in the estimation of nitrogen attainable by Will a. Varrentrapp's method of combustion with soda-lime, and by the method of combustion with copper oxide and collection of the nitrogen as gas, in the manner recommended by Dumas (i. 242). According to the majority of chemists who have published their experience of the two methods, the soda-lime process, when applied to substances which are difficult to burn, such as albuminoids, meat and other animal matters, or to those in which the proportion of nitrogen is small, as in milk-residues, manures, &c., gives results lower than those which are obtained by the process of Dumas. (See Nowak, *Wien. Akad. Ber.* [2 Abth.], lxiv. 359–376; Seegen a. Nowak, *J. pr. Chem.* [2], vii. 200; *Zeitschr. anal. Chem.* 1874, 460; Kessler, *Pharm. J. Trans.* [3], iii. 328; Bobierre, *Compt. rend.* lxxx. 960; Musso, *Gazz. chim. ital.* 1876, 391, and *Zeitschr. anal. Chem.* 1877, 406; C. Liebermann, *Liebig's Annalen*, clxxi. 103.) According to M  rker, on the other hand (*Zeitschr. anal. Chem.* 1875, 325), the errors in the estimation of nitrogen in gluten and meat by the soda-lime method are insignificant, provided the analysis be conducted carefully and with soda-lime free from magnesia. Ritthausen also (*J. pr. Chem.* [2], viii. 10) finds that this process gives results quite equal in accuracy to those obtained by Dumas' method, provided the substance be finely pulverised and the ammonia be determined, not by titration, but by precipitation as platinochloride. (See also Kreusler, *Ber.* vi. 1407; *Jahresb. f. Chem.* 1873, 916.) In the estimation of nitrogen in horn, leather, and wool-refuse, E. A. Grote (*Ber.* xi. 1558) recommends that the substance be dissolved in warm concentrated sulphuric acid before heating with soda-lime, the results thus obtained being higher than those given by the ordinary process.

A modification of Dumas' method is described by A. Dupr   (*Bull. Soc. Chim.* [2], xxv. 244), and a modification of Maxwell Simpson's apparatus (i. 243) by W. Hanks (*Ber.* xii. 451; *Chem. Soc. J.* xxxvi. 554).

Nitrogen Iodide is formed on adding iodine to white precipitate in presence of alcohol; but the reaction may be prevented by the addition of a small quantity of

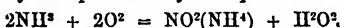
phenol (O. Rice, *Pharm. J. Trans.* [3], vi. 765). According to Champion a. Pellet (*Bull. Soc. Chim.* [2], xxiv. 447), nitrogen iodide explodes in contact with chlorine or bromine.

NITROGEN OXIDES. *Formation.*—Elaborate experiments by Carius (*Liebig's Annalen*, clxxiv. 1, 31; *Deut. Chem. Ges. Ber.* vii. 1481) have shown that, contrary to the generally received opinion, free nitrogen is not oxidised by ozone in presence of water, either at ordinary or at higher temperatures (120° – 210°), no acids of nitrogen being formed in any case. The alleged formation of ammonium nitrite by the evaporation of water or the condensation of aqueous vapour in air was tested by causing purified air to stream through water in a retort heated to temperatures ranging from 45° – 100° ; but not the least trace of a nitrogen-acid was formed, even though each experiment was continued for several days.

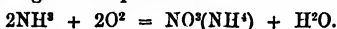
Schönbein found (1849) that lime-water through which a mixture of nitrogen and ozonised oxygen has been passed contained oxygen-acids of nitrogen. Berthelot, however, points out that lime-water prepared from ordinary lime contains appreciable quantities of calcium nitrate. To avoid this source of error, he passed the same gaseous mixture through pure baryta-water, and found that not a trace of nitrous or nitric acid was produced. On the other hand, he confirms the observation of Schönbein that nitrous acid is formed during the slow oxidation of phosphorus in the air (*Compt. rend.* lxxxiv. 61).

The experiments of Carius have rendered it probable that a principal source of the formation of nitrogen oxides is the oxidation of ammonia by ozone. Electrolytic oxygen containing from 2 to 3.5 v. p. c. of ozone passes through dilute aqueous ammonia for the most part unaltered, appearing, indeed, not to be absorbed by it more than by pure water. If, however, the solution be very dilute (1 : 2500), a thick white cloud forms above the liquid, consisting of products of oxidation mixed with excess of ozone; this cloud is especially thick with somewhat stronger ammonia, and disappears only when the ammonia is extremely dilute. The best mode of proceeding is to pour a solution of 0.02 to 0.03 grm. ammonia in 50 c.c. of water into a narrow glass cylindrical vessel, the neck of which forms a narrow glass tube 0.6 met. long, so that the absorption may be promoted by the long column of liquid and the drops of water in the long neck; it is also favoured by cooling with ice. Nevertheless, such an experiment requires the continuation of a stream of richly ozonised oxygen (evolved by 12 to 16 Bunsen's cells) for twenty to thirty hours, inasmuch as the greater part of the ozone passes through unaltered. In this manner a solution is obtained which is mostly very faintly alkaline, but sometimes neutral or even slightly acid.

Numerous and exact experiments have shown that this solution contains nitrous acid, nitric acid, and hydrogen dioxide. The formation of the nitrous acid and hydrogen dioxide may be represented by the equation:



That of ammonium nitrate may be explained in various ways: (1). By a simultaneous further oxidation of the nitrite by the ozone. (2). By the action of hydrogen dioxide on the nitrite. (3). On the assumption that the oxidation of the ammonia partly takes place according to the equation:



The second explanation is perhaps the most probable. Carius was of opinion that the oxidation of ammonia by ozone is perhaps the most important natural source of nitrous and nitric acids. The modes of formation of these acids in nature established by experiment are, according to Carius' investigations, the following:

a. From Free Nitrogen.

- (1). By electric discharge in the air.
- (2). By oxidation of other bodies in the air.

b. Oxidation of Ammonia.

- (1). By electric discharge.
- (2). By the presence of so-called alkaline substances.
- (3). By ozone.

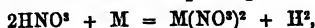
The efficacy of ozone as an oxidiser of ammonia (whereby nitrous acid, nitric acid, and water are produced) was also noticed by Goppelsroeder (*J. pr. Chem.* 1871, [2], iv. 139, 383). On the function of living organisms in promoting the oxidation of ammonia and organic nitrogen in the soil, see NITRIFICATION (p. 1400).

Reduction.—An elaborate research on the reduction of nitric acid and the oxides of nitrogen by various metals has been published by J. J. Acworth and H. E. Armstrong (*Chem. Soc. J.* 1877, xxxii. 54–90). The action of the metal on the nitric acid

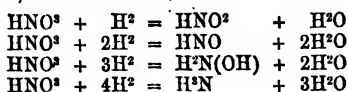
Action of Metals on Nitric Acid.

Weight of Metal	Temperature	Strength of acid	c.c. of Gas obtained	Percentage-composition of the Gaseous Mixture			c.c. of Gas per unit weight of Metal			
				NO	N ² O	N ²	Total	NO	N ² O	N ²
0.3215 Copper	15°	1 : 1	43.48	98.17	0.92	0.91	8574	8417	78	78
0.920 "	13	1 : 2	221.63	98.26	0.99	0.75	15272	15007	151	114
0.2885 "	90	1 : 2	51.40	97.23	1.82	0.95	14261	13866	259	136
0.329 "	12	1 : 4	63.27	94.28	3.57	2.15	12192	11494	435	263
0.325 "	16	1 : 8	66.16	71.89	20.74	7.37	12845	9234	2684	947
0.459 "	10	1 : 2 saturated with Cu ² NO ³	80.16	87.80	9.74	2.46	11072	9721	1078	273
0.410 "	13	1 : 2 and 5 g. NH ⁴ NO ³	114.52	30.92	1.96	67.12	17708	5475	348	11885
0.400 Silver	11	1 : 2	17.78	97.18	—	2.82	9601	9330	—	271
0.400 Zinc	5	1 : 8	35.33	46.05	49.86	4.09	5741	2643	2862	236
0.400 "	5	1 : 4	34.39	49.08	47.60	3.32	5588	2742	2659	187
0.400 "	7	1 : 2	31.30	45.30	49.90	4.80	5086	2304	2538	244
0.221 "	90	1 : 2	19.31	51.88	39.99	8.13	5679	2946	2271	462
0.3455 "	15	1 : 1	22.38	31.23	59.56	9.21	4210	1814	2507	389
0.321 "	15	1 : 0	15.68	0.95	78.29	20.76	3175	31	2485	659
0.179 "	12	1 : 4 and saturated with NH ⁴ NO ³	48.35	—	2.97	97.03	17557	—	521	17036
0.3655 Cadmium	13	1 : 2	35.05	79.00	17.74	3.26	10740	8485	1905	350
0.3085 Magnesium	12	1 : 2	67.81	17.87	61.55	20.58	5271	944	3246	1085
0.251 Iron	16	1 : 1	54.22	91.68	1.28	7.04	8064	7392	104	567
0.3975 ₂ "	13	1 : 2	63.86	98.77	6.26	4.97	5997	5323	375	299
0.400 "	10	1 : 4	57.12	86.27	9.50	4.14	5330	4598	551	221
0.318 "	12	1 : 8	50.30	93.87	3.43	2.0	5904	5542	202	160
0.200 "	9	1 : 12	30.81	91.28	4.45	4.27	5638	5146	252	242
0.2355 Nickel	13	1 : 2	7.76	5.37	83.31	11.32	1935	104	1612	219
0.4295 Cobalt	18	1 : 2	7.78	5.71	79.23	15.06	1090	63	863	164
0.265 Iridium	15	1 : 2	29.43	90.57	4.49	4.94	8395	7603	376	416
0.141 Aluminium	60 to 65	1 : 1	78.4	97.0	0.7	2.3	15290	14331	—	—
0.4135 Tin	14	1 : 0	21.54	1.08	85.14	13.78	3073	34	2616	423
0.414 "	15	1 : 1	31.02	16.35	73.82	9.80	4420	724	3263	433
0.404 "	11	1 : 2	35.17	22.37	67.78	9.85	5136	1148	3481	508
0.415 "	11	1 : 8	4.66	3.27	85.02	11.80	3312	106	2816	390
0.381 Lead	14	1 : 2	10.56	51.23	41.47	7.30	5737	2939	2379	419
0.3065 Thallium	30	1 : 2	6.42	69.78	19.15	11.07	8546	5963	1046	947

is supposed to consist, in the first instance, in the replacement of the hydrogen of the acid by the metal, and formation of the corresponding nitrate:



the hydrogen, however, not being in any case evolved as gas, but acting on the free acid present, and reducing it more or less completely to nitrous acid, hyponitrous acid, hydroxylamine, and ammonia.



Lastly, the gaseous products which are given off in the solution of metals in nitric acid arise from the decomposition and mutual action of the reduction-products above mentioned. The nitrogen dioxide evolved results chiefly, if not wholly, from the decomposition of nitrous acid:



it is, however, likewise possible that the dioxide may be produced by oxidation of the hyponitrous acid and the hydroxylamine by the nitric acid. The monoxide, N^2O , is produced either by decomposition of the hyponitrous acid, HNO , or by the action of nitrous acid on hydroxylamine. Lastly, the nitrogen which is given off in the free state may be regarded as a product of the action of nitrous acid on ammonia.

The verification of these theoretical deductions requires an exact study of the mutual action of the various reduction-products under all possible conditions; and as a first stage in this extensive research, Acworth and Armstrong have made a special study of the gaseous products of the action of metals on nitric acid, the main results of which are embodied in the table on p. 1407.

Monoxide and Hyponitrous Acid. According to Favre (*Ann. Chim. Phys* [5], i. 209), the heat evolved in the absorption of nitrogen monoxide by charcoal amounts to 3718 and its heat of liquefaction to 222.2 gram-degrees.

Hyponitrous acid, HNO , which Divers obtained by reducing a solution of potassium or sodium nitrate with sodium-amalgam (vii. 853), is, according to Zorn (*Deut. Chem. Ges. Ber.* x. 1306), more easily prepared by reduction of the nitrite. The resulting solution, after acidulation with acetic acid, gives, with silver nitrate, a greenish-yellow precipitate of silver hyponitrite which, by solution in dilute nitric acid and gradual precipitation with ammonia, is easily obtained of pure yellow colour. It may be dried over sulphuric acid, and may be heated for some time at 100° without alteration. When heated with acetic acid, it is resolved into silver acetate and nitrogen monoxide. It acts on alcoholic iodides, in some cases with violence. According to Van der Plaats (*ibid.* 235), this salt is not decomposed by diffused daylight; it is insoluble in water, and may be boiled therewith without decomposing. It decomposes when heated above 110° , and if it be quickly heated to 150° , the decomposition is accompanied by explosion and emission of brown vapours. It dissolves readily in dilute nitric or sulphuric acid, but is reprecipitated on neutralisation. It is not decomposed by carbonic acid, and caustic soda-ley does not attack it till heated to 70° . It is decomposed by phosphoric acid, acetic acid, hydrogen sulphide, and especially by hydrochloric acid, with liberation of hyponitrous acid, which is thus obtained in the form of a colourless solution having a strong acid reaction, and forming a yellow precipitate with silver nitrate. The solution is moderately stable, and may even be boiled with acetic or nitric acid without decomposing. It colours a mixture of potassium iodide and starch, and reduces permanganate. Strong sulphuric acid decomposes the acid and its silver salt, with evolution of nitrogen monoxide. The same decomposition takes place spontaneously when the aqueous solution is left to itself for a considerable time.

Sodium hyponitrite, $\text{NaNO} + 3\text{H}^2\text{O}$, crystallises in white needles. Its solution gives, with copper salts, a turquoise-blue precipitate; with magnesium, manganese, zinc, barium, strontium and calcium salts, white precipitates soluble in acetic acid; with bismuth, aluminium, lead, tin, and cerium salts, white precipitates insoluble in acetic acid; with cobalt chloride a red, with nickel sulphate a greenish-white, and with mercuric chloride a white precipitate easily changing to brown; with mercurous hydroxide a black, with ferrous sulphate an olive-green, with ferric chloride a yellow precipitate. From gold-solution it reduces the metal; with platonic chloride it forms a reddish-white precipitate. By heating the silver salt with ethyl iodide, an ethyl hyponitrite is obtained (Menke, *Chem. Soc. J.* xxxiii. 401).

Dioxide, NO or N^2O^2 . On the liquefaction of this gas, see GASES (p. 857).

A lecture experiment to demonstrate the direct combination of nitrogen dioxide with oxygen, and the reaction of the resulting tri- and tetroxide with water, is described by G. Bruylants (*Deut. Chem. Ges. Ber.* ix. 7; *Chem. Soc. J.* xxix. 878).

Nitrogen dioxide may be utilised for the regeneration of manganese residues. Manganous nitrate, heated to 200°, leaves a residue of pure manganese dioxide, and if the evolved gases, mixed with a sufficient quantity of air, be passed into precipitated manganous hydroxide, a fresh quantity of nitrate will be produced, which may be decomposed by heat as before, and so on. Nitrogen dioxide is never reduced by manganous hydroxide to the monoxide or to free nitrogen (Kuhlmann, *Dingl. pol. J.* cexi. 25).

Reaction with Pyrogallol.—Nitrogen dioxide is decomposed by an alkaline solution of pyrogallol, more than 50 per cent. of it disappearing and being replaced by monoxide and free nitrogen. As, however, the same reaction is produced after some time by an alkaline solution of pyrogallol which has become completely saturated with oxygen by prolonged contact with the air, and likewise with potash-loy, as observed by Gay-Lussac,—and, moreover, as even pure water, when heated for a long time with nitrogen dioxide in sealed tubes, effects its conversion into nitrous acid, nitrogen monoxide, and free nitrogen,—and as, on the other hand, pure pyrogallol exerts no action on nitrogen dioxide, it seems probable that the change under consideration is due, not to the alkaline pyrogallate, but to the gradual action of the excess of alkaline hydrate present, or perhaps to that of products formed by the action of oxygen on pyrogallol. For gas analysis, these observations have a practical value, inasmuch as they show that a contraction of volume ensuing on the introduction of alkaline pyrogallol into a measured quantity of air is not necessarily due to the presence of oxygen (Russell & Lapraik, *Chem. Soc. J.* xxxii. 35).

Trioxide, N₂O₃. On the formation of this Oxide and of Nitrous Acid and Ammonium Nitrate in the soil, &c. see p. 1406.

On the constitutional formulæ of Nitrogen Trioxide and of the Nitrites, see Günsberg (*Wien. Akad. Ber.* lxviii. 498; *Jahresb. f. Chem.* 1873, 218).

On the Colouring Matters produced by the action of Nitrous Acid upon Phenol, and on Liebermann's reaction, see vii. 901; viii. 697.

Detection and Estimation of Nitrous Acid.—E. Kopp (*Deut. Chem. Ges. Ber.* v. 284; *Chem. Soc. J.* xxvi. 91) recommends diphenylamine as a test for nitrous acid. To prepare the reagent, pure sulphuric acid is poured over a few crystals of diphenylamine, and a little water is added, whereby a clear solution is obtained which produces with nitrous acid a very fine and permanent blue colour. The reaction is at least as delicate as that with ferrous sulphate.

To detect the presence of nitrous acid in waters, H. Kämmerer (*Jahresb. f. Chem.* 1874, 964) adds to 500 c.c. of the water 1 c.c. of thick starch-paste, a granule of potassium iodide, a pinch of zinc-dust, and finally a quantity of dilute acetic acid (sp. gr. 1.04) sufficient to produce a strong acid reaction. The production of a blue colour indicates the presence of nitrous acid. Sulphuric acid must not be used in place of acetic acid, since it would decompose any nitrates present in the liquid, and the nitric acid thereby set free might be reduced to nitrous acid by organic matter. If, however, nitrous acid is known to be absent, the starch-paste mixture above described may serve for detection of nitric acid by the simple addition of sulphuric acid. According to Fresenius, this method is not sufficiently delicate for the detection of small quantities of nitrous acid in waters; but satisfactory results may be obtained by acidifying the liquid with acetic acid and distilling. The nitrous acid then passes over undecomposed in the first portions of the distillate, and may be determined by permanganate solution. This method has the advantage of insuring the absence of non-volatile compounds, which might decompose the iodised starch.

F. Fischer (*Dingl. pol. J.* cexii. 404) considers this last method as the most delicate and exact of any that have been proposed for the estimation of nitrous acid in potable waters.

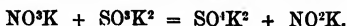
METALLIC NITRITES. Observations on the occurrence of these salts in plants have been made by P. Genadius (*Amer. Chem.* v. 7). The characteristic blue colour with potassium iodide, starch-paste, and sulphuric acid was immediately exhibited by the juice of *Lactuca sativa*, *Lycopersicon esculentum*, *Taraxacum Dens Leonis*, *Dahlia variabilis*, *Batata edulis*; gradually and faintly by that of *Solanum pseudo-capsicum*, *Plantago major*, *Daucus Carota*, *Solanum tuberosum*; not at all by that of *Asparagus officinalis*, *Rheum raphaniticum*, *Vitis labrusca*, *Cannabis sativa*, or *Zea Mays*. The bluing is for the most part produced only by the fresh juice, not by juice a few minutes old; sometimes, however, by juice twenty-four hours old.

Ammonium Nitrite, NH⁴.NO².—Worth & Weber (*Deut. Chem. Ges. Ber.* vii. VOL. VIII.

1745) confirm the statement of Carius that ammonium nitrite is never formed by the direct combination of water and nitrogen. Berthelot finds, however, that this salt is produced when perfectly pure nitrogen gas and water are enclosed between two concentric tubes and subjected to the action of a very powerful Ruhmkorff's coil, but that this effect is not produced by weak electric currents (*Bull. Soc. Chim.* [2], xxvii. 338). Zöller u. Grote (*Deut. Chem. Ges. Ber.* x. 2145) confirm the statement of Schönbein (*Jahresb. f. Chem.* 1862, 94), which was doubted by Bohlig (*ibid.* 1863, 167) that ammonium nitrite is formed during the combustion of perfectly pure hydrogen in perfectly pure atmospheric air.

On the formation of this salt by oxidation of ammonia, see p. 1406; on its production, together with hydrogen dioxide, when a dilute solution of pyrogallol is exposed to the air, see p. 1071.

Potassium and Sodium Nitrites may be prepared by fusing the corresponding nitrates with equivalent quantities of dried potassium or sodium sulphite:



The cooled mass is pulverised, and the nitrite is purified by extraction with alcohol or by crystallising out the sulphate (Etard, *Bull. Soc. Chim.* [2], xxvii. 434). The sodium salt is recommended by C. Lieber (*Dingl. pol. J.* cccix. 245) as an antichlor, instead of the thiosulphate, as it has the advantage of not depositing sulphur in the pores of the tissues. 100 parts of it are capable of counteracting the action of 103 pts. of chlorine; 100 pts. of the thiosulphate neutralise 114.4 chlorine.

Lead Nitrites.—The basic nitrites of lead have been examined by F. Meissner (*Jenaische Zeitschrift*, [2], iii. 26). The red salt obtained by boiling 1 pt. normal lead nitrate with 1½ pt. granulated lead and 50 pts. water was regarded by Berzelius as NO^4HPb^2 or $4\text{PbO} \cdot \text{N}^2\text{O}^2 \cdot \text{H}^2\text{O}$ (iv. 73). Meissner finds that, after repeated crystallisation from water perfectly freed by boiling from air and carbonic acid, it has the composition $\text{N}^2\text{O}^2\text{Pb}^2 \cdot \text{H}^2\text{O}$ or $3\text{PbO} \cdot \text{N}^2\text{O}^2 \cdot \text{H}^2\text{O}$ or $2\text{PbO} \cdot (\text{NO}^2)^2\text{Pb} \cdot \text{H}^2\text{O}$. The yellow basic nitrite, obtained by digesting 100 pts. lead nitrate with 78 lead, and water at 70°–75°, has, according to Meissner, the composition NO^4PbH^2 or $\text{PbO} \cdot (\text{NO}^2)^2\text{Pb} \cdot 3\text{H}^2\text{O}$.

Platinum Nitrites.—See PLATONITRITES, under PLATINUM.

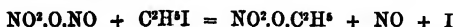
ALCOHOLIC NITRITES. NITROUS ETHERS. *Amyl Nitrite*, $\text{NO}^2(\text{C}^5\text{H}^{11})$.—For the preparation of this ether, A. Hilger (*Arch. Pharm.* [3], iv. 485) recommends passing nitrogen trioxide (from As^2O^3) into amyl alcohol heated to 60°–70°. The distillate is shaken with weak aqueous potash, then dehydrated and rectified. The pure ether has a pale yellow colour, sp. gr. = 0.902, and boils at 94°–95°. In contact with the air it easily decomposes, yielding nitrous acid, valeric acid, amyl alcohol, and amyl valerate. According to E. Rennard (*Russ. Zeitschr. Pharm.* 1874, 1), a good yield is obtained by distilling 30 pts. amyl alcohol with 26 pts. potassium nitrite dissolved in 15 pts. water and 30 pts. sulphuric acid.

Propyl Nitrite, $\text{NO}^2(\text{C}^3\text{H}^7)$, prepared by passing nitrogen trioxide into propyl alcohol, has a fragrant odour, sp. gr. = 0.935 at 21°, and boils at 43°–46° (Cahours, *Compt. rend.* lxxvii. 749).

Tertiary Butyl Nitrite, $\text{NO}^2\text{C}(\text{CH}^3)_3$, is formed, together with a small quantity of its isomeride, tertiary nitrobutane, $\text{C}(\text{NO}^2)(\text{CH}^3)_3$, by treating the corresponding butyl iodide with silver nitrite. It is a liquid boiling between 76° and 78°, and slightly soluble in water (Tscherniak, *Deut. Chem. Ges. Ber.* ix. 155).

Tetroxide, NO^2 or N^2O^4 . *Compound with Magnesium Phosphate*, $2\text{PO}^4\text{MgH} + \text{NO}^2$. This compound is prepared by dissolving magnesium pyrophosphate in nitric acid of sp. gr. 1.25; keeping the solution for some time near the boiling heat to convert the pyrophosphoric acid into orthophosphoric acid; then evaporating the liquid on the water-bath; reducing the white gummy fissured acid residue to coarse powder; and heating it for some time to a somewhat higher temperature, best on a paraffin bath, till it has become red-brown and no longer gives off acid vapours. As thus prepared, it is a crystalline powder, whitish-yellow at ordinary temperatures, turning rusty brown when heated, and recovering its whitish-yellow colour on cooling. At a higher temperature it gives off water and nitrogen tetroxide, and leaves magnesium pyrophosphate (E. Luck, *Zeitschr. anal. Chem.* 1874, 255).

Reactions.—Alcoholic iodides are converted by nitrogen tetroxide, with separation of iodine, into the corresponding nitrates, e.g. amyl iodide at 147°–150° into amyl nitrate, ethyl iodide at 83°–85° into ethyl nitrate. This reaction tends to confirm the view that liquid nitrogen tetroxide has the constitution $\text{NO}^2 \cdot \text{O} \cdot \text{NO}$, and is not easy to reconcile with the formula $\text{NO}^2 \cdot \text{NO}^2$:



(L. Henry, *Bull. Acad. Belg.* [2], xxxviii, 1). This view is also in accordance with Exner's observations on the reaction of nitryl chloride with silver nitrite (vii. 855). See, on the other hand, Günsberg (*Wien. Akad. Ber.* [2 Abth.], lxviii. 498; *Jahresb. f. Chem.* 1873, 218).

On the reaction of Nitrogen Tetroxide with *Boron Chloride*, see BORON (p. 342).

On the *Heat of Solution* of Nitrogen Tetroxide, see HEAT (p. 989).

Pentoxide, N_2O_5 . The following modification of R. Weber's method of preparing the pentoxide by the action of phosphoric anhydride on nitric acid (vii. 856) has been proposed by Berthelot (*Bull. Soc. Chim.* [2], xxi. 53). Phosphoric anhydride is added continuously and by small portions to somewhat less than an equal weight of hydrogen nitrate, NO^3H , cooled with ice and salt, care being taken that the temperature of the liquid never rises above 0° ; the thick mass is then introduced into a wide retort through the tubulus, and very slowly distilled, the retort being immediately cooled if the mass shows any tendency to froth over. The nitrogen pentoxide then passes over quite pure, and condenses in the receiver to large perfectly white crystals. Towards the end of the distillation, a small quantity of Weber's hemihydrate, $2N_2O_5 \cdot 11H_2O$, passes over. 150 grams of hydrogen nitrate thus treated yielded 80 grams of crystallised pentoxide. The latter may be kept in stoppered glass bottles placed under a bell-jar with sulphuric acid. When exposed to light, it is very quickly resolved into oxygen and the tetroxide.

Nitric Acid, NO^3H . *Occurrence in Rain-water.*—Observations on the quantities of nitric acid and ammonia in the rain-water which fell during the years 1870–71–72 at Florence and at a station on Vallombrosa, a spur of the Tuscan Apennines, 957 meters above the sea-level, have been published by E. Bechi (*Ber.* vi. 1203). The following are the results per hectare of surface:

	Florence			Vallombrosa
	1870	1871	1872	
Quantity of Rain in cubic meters	9284	10789	12909	20278
„ Ammonia in grams	13226	10572	12917	10433
„ Nitric Acid „	15728	9153	13057	11726

On the formation of Nitric Acid in nature by the oxidation of Ammonia and its non-formation by the oxidation of free Nitrogen, see p. 1406.

A process for the continuous formation of Nitric Acid from Ammonia by means of oxygen evolved from a mixture of Manganese Dioxide and Caustic Soda, is described by Schwarz (*Dingl. pol. J.* cxxviii. 219; *Chem. Soc. J.* xxix. 878).

On recent Improvements in the Manufacture of Nitric Acid, see H. Göbel (*Dingl. pol. J.* cxxix. 238; *Chem. Soc. J.* xxx. 238).

On the Thermal relations of Nitric Acid and the Nitrates, see HEAT (pp. 952–959, 965, 973, 981, 984, 987, 993, 995).

On the action of Nitric Acid upon Metals, see p. 406; on *Lead Chromate*, p. 461.

Detection. 1. With *Ferrous Sulphate*.—F. Bolas (*Chem. News*, xxviii. 248) recommends for the detection of nitric acid and nitrates, the use of a solution of *ferrous sulphate* in strong sulphuric acid, the liquid to be tested being carefully poured upon this solution by means of a pipette. The solution of ferrous sulphate is prepared by mixing the sulphuric acid with 10 v. p. c. of a cold saturated aqueous solution of ferrous sulphate, and heating it to boiling, in order to decompose any nitrogen-acids that may be present in the sulphuric acid.

2. With *Brucine*.—According to E. Reichardt (*Arch. Pharm.* cxlv. 108), the red colour which brucine produces with nitric acid is distinctly perceptible in a solution of 1 pt. potassium nitrate in 100,000 pts. of water, if to half a drop of the liquid to be tested there be added 1 or 2 drops of brucine-solution, and then gradually from a pipette a few drops of strong sulphuric acid. Böttger (*N. Rep. Pharm.* xxiii. 120) recommends this method for the detection of nitric acid or nitrates in potable waters, &c.

Testing of Nitric Acid for Iodine.—According to A. Hilger (*Arch. Pharm.* [3], vi. 391), the best method of detecting iodine (i.e. iodic acid) in nitric acid, is to dilute the acid with an equal volume of water, agitate it with carbon sulphide, and then add a small quantity of metallic tin. The tin then reduces the nitric acid to nitrogen dioxide and nitrous acid, both of which exert a strong reducing action on the iodic acid.

Estimation. (1). With *Indigo*.—The method given by Marx (vii. 858) for estimating nitric acid in well-water by means of indigo-solution has been modified by F. Fischer (*J. pr. Chem.* [2], vii. 57), in so far that the sulphuric acid is mixed with the indigo-solution and added by drops to the water, till a faint greenish tint is pro-

duced. By this mode of proceeding, the nitric acid is not set free to act on the organic matter in the water before the indigo-solution is added. Fischer also recommends that the standard indigo-solution should be prepared with indigo purified by precipitation or sublimation, as the impurities in commercial indigo interfere with the accuracy of the determination (*Dingl. pol. J.* ccxii. 404; ccxiii. 423).

The following observations on this method have been made by R. Warington (*Chem. News*, xxxv. 45, 57; xxxix. 285).

(1). The maximum amount of indigo is consumed only when a sufficiency of indigo is present with the nitrate before the addition of oil of vitriol. The plan adopted by Marx of mixing the nitrate solution with twice its volume of oil of vitriol, and then immediately running in the indigo, always consumes less indigo than the nitrate is capable of oxidising. The full amount of indigo can be ascertained only by a series of approximating experiments, in which the oil of vitriol is suddenly added to the previously mixed nitrate and indigo. (2). The amount of indigo required depends greatly on the proportion of sulphuric acid present, and within certain wide limits the amount of indigo is less as the proportion of sulphuric acid is greater. With 10 c.c. of nitre solution 11.3 c.c. of indigo were required, when the indigo and nitre were mixed with their own volume of oil of vitriol; but 8.9 c.c. of indigo were sufficient when two volumes of oil of vitriol were employed. (3). The full amount of indigo is consumed only when the temperature of the mixture remains sufficiently high during the reaction; 100°, 110°, and 120° are given by various writers as the minimum temperature. When the reaction is immediate, artificial heat is unnecessary; but when, through dilution of the nitrate, small volume of the liquid, weakness of the vitriol, &c., the reaction is tardy, the temperature of the flask containing the mixture must be maintained by a paraffin or chloride of calcium bath, or the results will be too low. (4). The true tint of final reaction is a dull brown, which precedes the commencement of green; the brown tint becomes green when suddenly diluted with water. If a solution of sublimed indigotin in sulphuric acid is employed, the tint passes at once from gold to green without an intermediate brown stage. (5). "When a nitrate solution is diluted, it apparently requires distinctly less indigo per unit of nitrate if a double volume of oil of vitriol be employed; but if a single volume is used, the difference is very slight, and in the contrary direction. If two volumes of sulphuric acid are employed, the indigo must, therefore, be standardised with nitre solutions of several dilutions to ascertain the value of different parts of the scale. (6). The influence of chlorides is slightly to diminish the indigo required. With .03 to .10 gram of chloride of sodium in 10 c.c. of nitre solution, the reducing effect of 100 chloride of sodium was equal to 1.16 nitre. With much chloride the final tint is a bright green. (7). Some kinds of organic matter have a powerful reducing action. Cane-sugar had a greater effect the larger the proportion of sulphuric acid and the more dilute the nitrate; with a $\frac{1}{10}$ th nitre solution, and a double volume of oil of vitriol, 100 of sugar had a reducing effect equal to 62.3 nitre. The soluble humic matter of soils was apparently without influence, determinations of nitrate in a kitchen garden soil by the mercury method and by the indigo method giving accordant results: only 1 vol. of sulphuric acid was used in this experiment. (8). Nitrites cannot be determined by indigo: they oxidise less indigo than nitrates, and do not give a sharp reaction; they must be converted into nitrates by permanganate before employing the indigo. For details of the experiments on which these conclusions are founded, see *Chem. Soc. J.* xxxv. 578-589.

(2). *Estimation of Nitric Acid as Nitrogen Dioxide by means of its action on Mercury.*—This method, introduced by W. Crum (iv. 88) and improved by Frankland, has also been tested by Warington (*Chem. Soc. J.* xxxv. 375), who finds that, in the absence of organic matter, and with proper manipulation, it is susceptible of great accuracy, and is capable of determining extremely small quantities of nitrates and nitrites. The natural error of the process is one of deficiency. The presence of chlorides in moderate quantity is no hindrance: quantities of organic matter, small in relation to the nitrates present, have little or no effect on the results; larger quantities, especially of cane-sugar, may cause a considerable deficiency, which is reduced, but not entirely removed, by the presence of chlorides.

(3). *By Conversion into Ammonia.*—a. A mode of estimation founded on the conversion of nitric acid into ammonia through the agency of the copper-zinc couple (vii. 454; viii. 568), is given by T. E. Thoms (*Chem. Soc. J.* xxvi. 541). When a strip of zinc, coated with finely divided copper (p. 568), is immersed in water containing potassium nitrate, no evolution of hydrogen takes place, but a smell of ammonia becomes perceptible and free alkali is produced. The conversion of nitric acid into ammonia thus effected is complete with the nitrates of potassium, sodium, calcium, lead, and probably also with those of silver, mercury, copper, thallium and

all other metals which are reduced by zinc, so that in these cases it may be made the foundation of a quantitative estimation of nitric acid in well-waters, &c. The reduction appears to be most difficult in the case of ammonium nitrate. The result may also be affected by the concentration of the solution and the quantities of zinc and copper employed. If the solution is too strong, nitrogen tetroxide will be evolved, and if the quantities of zinc and copper present are insufficient, the reduction will be imperfect. β . Piuggari (*Compt. rend.* lxxvii. 481) digests the substance under examination (waters, soils, manures) for two or three hours at 50° – 60° with a mixture of silver chloride and potash, whereby the whole of the nitrogen present is converted into ammonia, nitric acid, and nitrous acid, and reduces the two latter completely to ammonia with aluminium-foil and potash. The ammonia is then determined colorimetrically by Nessler's test, or with phenol and sodium hypochlorite. γ . Fr. Gramp (*J. pr. Chem.* [2], xi. 72), from a comparison of the various methods which have been proposed for the estimation of nitric acid, concludes that the conversion of the acid into ammonia by means of sodium-amalgam is the quickest and most exact.

A comparison of the various methods which have been proposed for the estimation of nitric acid, with suggestions for ensuring greater accuracy, is given by J. M. Eder (*Zeitschr. anal. Chem.* 1877, 267–314; abstr. *Chem. Soc. J.* xxxii. 643); also by G. Lunge (*Ber.* x. 1073; *Chem. Soc. J.* xxxii. 642).

On the estimation of Nitric Acid in Chili Saltpetre and commercial Nitrates in general, see F. Jean (*Bull. Soc. Chim.* [2], xxvi. 10; *Jahresb. f. Chem.* 1876, 979).

Valuation of Alkaline Nitrates.—H. Joulie (*Compt. rend.* lxxvi. 230) converts these salts into chlorides by ignition with sal-ammoniac, and determines the chlorine before and after this operation by titration with silver nitrate and potassium chromate. The difference between the two determinations gives the quantity of chlorine which has taken the place of the nitric acid, and this number multiplied by 1.52 gives the amount of nitric acid in the nitrate under examination. In the valuation of sodium nitrate, the weight of the mass after ignition should come very near to that which is obtained by converting the total quantity of chlorine found into sodium chloride. If it comes out more than 0.5 or 0.75 times as great as this number, the foreign ingredients must be determined quantitatively. In the case of potassium nitrate, the quantity of chlorine originally present, reckoned as sodium chloride, and the quantity of chlorine equivalent to the nitric acid reckoned as potassium chloride, should together give a number somewhat smaller than the weight of the ignited mass. Should it be equal to or greater than the latter, the presence of sodium nitrate must be assumed, and a quantitative estimation of the potash must be made.

METALLIC NITRATES.

Ammonium Nitrate, NH_4NO_3 .—G. Tissandier (*Compt. rend.* lxxxii. 388) has described and figured the microscopic appearance of the crystals which remain on leaving rain-water to evaporate. These crystals, which Tissandier regards as ammonium nitrate, exhibit an extraordinary diversity of shape, which he attributes to the simultaneous presence of organic substances, since very dilute solutions of ammonium nitrate artificially prepared leave, on spontaneous evaporation, crystals of only one kind.

Observations on the decomposition of ammonium nitrate by heat have been made by Berthelot (*Compt. rend.* lxxxii. 932). The salt melts at about 152° , but does not begin to decompose rapidly till heated to about 210° . Above this point, the decomposition goes on with increasing rapidity as the temperature rises, and above 300° it becomes explosive. The quantity of nitrogen monoxide evolved in this decomposition is always below that indicated by theory, because a considerable proportion of the salt volatilises undecomposed. Ammonium nitrate may indeed be volatilised without appreciable decomposition by introducing the previously fused salt into a basin covered with filter-paper, and placing above this cover a cylinder of stouter paper filled with coarse fragments of glass. On slowly heating the basin on a sand-bath, not above 190° – 200° , the salt sublimes in beautiful shining crystals, which collect on the sides of the basin or on the lower surface of the paper. Part of it also passes through the filter-paper and condenses in the form of a white deposit. As the temperature of the paper traversed by the salt may rise above 130° without any sign of alteration in the paper, Berthelot infers that the ammonium nitrate in this experiment volatilises as a whole, and is not resolved into nitric acid and ammonia, since the paper could scarcely remain in contact with free nitric acid at so high a temperature without immediate destruction.

The action of ammonia on ammonium nitrate, and the properties of the resulting ammoniated ammonium nitrate have been studied by F. Raoult (*Compt. rend.* lxxvii.

788) with results nearly the same as those obtained by Divers (vii. 859). Ammonia-gas is rapidly absorbed by the nitrate at all temperatures between -15° and $+25^{\circ}$, forming a colourless liquid, the composition of which varies with the temperature; when heated above 25° , it gives off ammonia and solidifies. 100 pts. ammonium nitrate under a pressure of 760 mm. absorb the following quantities of ammonia-gas:

Temperature	NH ³ absorbed	State of Aggregation
-10°	42.56	Liquid
0	35.00	"
+12	33.00	"
18	31.50	"
28	23.25	"
29	20.90	Solid
30.5	17.50	"
40.5	6.00	"
79	0.50	"

At -10° the liquid has the composition $\text{NH}_4\text{NO}_3.2\text{NH}_3$. It does not solidify in a mixture of ice and salt. Sp. gr. = 1.05. It easily gives off ammonia when heated, and the solid compound, obtained by heating it to 28.5° , has the composition $\text{NH}_4\text{NO}_3.\text{NH}_3$. By heating the liquid compound in a sealed bent tube, it is easy to obtain large quantities of liquid ammonia, 1 vol. of the liquid yielding about $\frac{1}{2}$ vol. of the liquefied gas, and leaving a residue of $\text{NH}_4\text{NO}_3.\text{NH}_3$.

Barium Nitrate, $\text{Ba}(\text{NO}_3)_2$.—This salt, as first observed by Scacchi (*Jahresh. f. Chem.* 1860, 13), crystallises in tetartohedral forms, the octohedral faces which occur on it easily splitting up into a predominant and a subordinate octohedron. The stripe-like elevations and corrosion-figures on the cubic faces of the crystals likewise indicate their tetartohedral development (H. Baumhauer, *Zeitschr. Kryst.* i. 51; W. J. Lewis, *Phil. Mag.* [5], iii. 453).

The product of decomposition of this salt by heat consists, according to Rammelsberg, not of barium monoxide, as hitherto supposed, but of a higher oxide, $\text{Ba}_2\text{O}^4 = 2\text{BaO} + \text{BaO}_2$ (p. 143).

Bismuth Nitrates.—The decomposition of these salts by water has been examined by Yvon (*Compt. rend.* lxxxiv. 1164). The crystallised nitrate, formed either with or without excess of acid, or by evaporating the wash-water which has served for the preparation of the basic nitrates, has always the same composition, viz. $\text{Bi}(\text{NO}_3)_3 + 5\frac{1}{2}\text{H}_2\text{O}$. When dried at temperatures above 100° , it gives off nitric acid as well as water, whence probably arise the discordant statements that have been made respecting the amount of water contained in it. When heated for some time in an oil-bath to 120° , it gives off water and acid and leaves a white pulverulent basic salt, $\text{Bi}_2\text{N}_2\text{O}^3 + 1\frac{1}{2}\text{H}_2\text{O}$. The same composition belongs also to the basic salts produced by the action of water or of the carbonates of the alkaline earths on the normal nitrate. The basic salt thus separated dissolves, as is well known, in a very large quantity of water; and Yvon finds that the solution thus formed deposits, in the course of several weeks, small prismatic crystals having the composition $\text{Bi}_2\text{N}_2\text{O}^3 + \frac{1}{2}\text{H}_2\text{O}$. These crystals, according to measurements by Des Cloizeaux (*Compt. rend.* lxxxiv. 1162), belong to the asymmetric or triclinic system. Their principal angles are:

$$\begin{aligned} (110)(\bar{1}\bar{1}0) \text{ or } \infty P : \infty P = 57^{\circ} 20'; & \quad (001)(110) \text{ or } 0P : \infty P = 56^{\circ} 25'; \\ (001)(\bar{1}\bar{1}0) \text{ or } 0P : \infty P = 67^{\circ} 8'. \end{aligned}$$

The plane of the optic axes is exactly parallel to the edge $(110)(100)$ or $\infty P : \infty \bar{P} \infty$. When the basic salt separated by water is repeatedly washed with water or with an alkaline carbonate, the compound $5\text{BiONO}_3.3\text{Bi}_2\text{O}^3 + 5\frac{1}{2}\text{H}_2\text{O}$ is obtained (Yvon). Similar results with regard to the decomposition of normal bismuth nitrate have been obtained by A. Ditte (see CHEMICAL ACTION, p. 427).

Cadmium Nitrate, $\text{Cd}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$.—The sp. gr. of this salt is 2.450 at 14° , and 2.460 at 20° (H. Laws, *Sill. Am. J.* [3], xiv. 281).

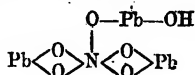
Copper Nitrate, $\text{Cu}(\text{NO}_3)_2$.—When a saturated solution of this salt is separated by a diaphragm of parchment-paper from a solution of potassium oxalate, there is formed, on the side of the paper in contact with the latter, a crystalline deposit of potassium-cupric oxalate, while potassium nitrate enters into the copper solution (Becquerel, *Compt. rend.* lxxvi. 245).

Didymium Nitrate, $\text{Di}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$. See DIDYMIUM (p. 643).

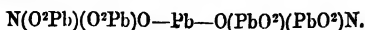
Lanthanum Nitrate, $\text{La}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$. See LANTHANUM (pp. 423, 1164).

Lead Nitrates.—The *hexplumbic nitrate*, $5\text{PbO}. \text{PbN}_2\text{O}^6.\text{H}_2\text{O}$ or Pb^6HNO_6 ,

which Berzelius obtained by precipitating the normal salt with excess of ammonia (iv. 96), may be regarded as a derivative of ortho-nitric acid, $N(OH)^2$, and represented by the formula :



or in the anhydrous state :



Heated to 170° in a sealed tube with ethyl iodide, it does not yield the corresponding pentethylic nitrate, but is converted, with formation of ethyl oxide and lead iodide, into normal lead nitrate, together with a small quantity of tetraplumbic nitrate (Meissner, *Jenaische Zeitschrift*, [2], iii. zweites Suppl.-Heft. 26).

Mercurous Nitrate is decomposed by hydrogen-potassium sulphide, with precipitation of metallic mercury, the supernatant liquid acquiring a yellow colour from formation of a polysulphide of potassium (J. Myers, *Deut. Chem. Ges. Ber.* vi. 440).

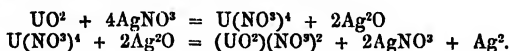
Nickel Nitrate.—A solution of this salt is recommended by H. Emsmann (*Pogg. Ann. Ergänzbd.* vi. 334) as an absorption-preparation. Its spectrum is entirely destitute of the extreme colours, red and violet.

Potassium Nitrate, KNO^3 .—This salt is contained in considerable quantity in the leaves of the castor-oil plant.

On its formation in the soil by the influence of organised ferments, see NITRIFICATION.

Experiments on the function of ferric oxide in the formation of saltpetre have been made by L. Pesci (*Gazz. chim. ital.* 1875, 307). The observation that saltpetre very generally effloresces from walls of ochreous bricks, led to the inquiry whether its formation arose from the oxidation of ammonia by the ferric oxide to which the colour of these bricks is due. It was found that ferric oxide, after being exposed to ammoniacal vapours for about six days, at 20° – 30° , and then exhausted with water, yielded a solution containing both nitric and nitrous acids. That this effect was not due merely to the porosity of the oxide, was shown by the same effect being produced in an atmosphere of carbonic anhydride containing ammonia, with partial reduction of the oxide. The reduction was more abundant when the action took place under a layer of water. The peculiar fertilising effects of composts containing ferric oxide is due to this property of ferric oxide, and for a similar reason ochreous chalk is preferable in forming an artificial nitre bed. Several samples of nitre have been found by Pesci to contain nitrites. The same observation was made by Böttger in 1869, in purified as well as in crude saltpetre.

Silver Nitrate, $AgNO^3$.—Uranous oxide, added to a solution of this salt, throws down metallic silver, the reaction taking place by two stages: first a salt of uranous oxide and argentous oxide is formed, and then the uranous salt is converted into uranyl salt, the colour of the solution changing from green to yellow, and at the same time the argentous oxide is reduced to metallic silver:



Silver is also precipitated from the nitrate, though very slowly, by the oxide U^3O^8 (Isambert, *Compt. rend.* lxxx. 1087).

On the reaction of silver nitrate with *hydrogen*, see vii. 660.

Double Salts.—When a solution of the nitrates of silver and potassium, containing more than an equivalent of silver nitrate, is evaporated, a double salt separates out, having the composition $AgNO^3.KNO^3$. With ammonium nitrate a similar compound is formed, an excess of silver nitrate, however, being unnecessary. With sodium, lithium, and lead nitrates no double salts are formed. On evaporating solutions containing equivalent quantities of silver nitrate and of sodium or lithium nitrate, no double salt is formed, but the silver salt separates out first, though it is much more soluble than the nitrate of the alkali-metal. With lead nitrate, also, no double salt is formed, but the lead salt, which is less soluble than the silver nitrate, is the first to crystallise out.

The crystals of the potassium and ammonium double salts are monoclinic. Axial ratio $a : b : c = 1.405 : 1 : 1.646$. Acute angle of axes = $82^\circ 22'$. Double refraction negative. The optic axes lie in a plane perpendicular to the plane of symmetry, their divergence for red light being about $4^\circ 25'$; for blue light $13^\circ 11'$. Strontium nitrate containing silver nitrate crystallises in cubo-octohedrons (Russell a. Maskelyne, *Proc. Roy. Soc.* xxvi. 357).

Vanadium Nitrate. See VANADIUM.

Zinc Nitrate, $\text{Zn}(\text{NO}_3)_2$.—When nitric acid is treated with a considerable excess of pure zinc, a basic salt is formed having the composition $\text{Zn}^{\text{H}}\text{H}^{\text{N}}\text{O}^{\text{H}} = \text{Zn}(\text{NO}_3)_2 \cdot 5\text{Zn}(\text{OH})_2 + 3\text{H}_2\text{O}$. When a neutral solution of zinc nitrate is evaporated to a syrup, the whole solidifies to a vitreous mass, which, when treated with water, is converted, with rise of temperature, into a vitreous basic salt. The vitreous mass has, according to Ordway, the composition $4\text{ZnO} \cdot 3\text{N}^{\text{O}} \cdot 3\text{H}_2\text{O}$ or $\text{ZnO} \cdot 3\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (iv. 107); according to Bertels, however, it is not of constant composition. The basic salt obtained by treating it with water was found by Bertels to consist of $\text{Zn}^{\text{H}}\text{H}^{\text{N}}\text{O}^{\text{H}} = 4\text{Zn}(\text{NO}_3)_2 \cdot 3\text{Zn}(\text{OH})_2 + 11\text{H}_2\text{O}$ (*Jahresb. f. Chem.* 1874, 274).

NITRIC ETHERS. According to J. Champion (*Compt. rend.* lxxiii. 571, 573; lxxviii. 1150), the nitric ethers of the fatty series may be prepared by the action of a mixture of nitric and sulphuric acids on the corresponding alcohols (vii. 860) or their acid sulphates, the proportions of the acid mixture being varied for the several alcohols. Methyl and ethyl alcohol react best with a mixture of 1 pt. nitric and 2 pts. sulphuric acid; the higher alcohols of the series with 1 nitric to 3 sulphuric acid.

Dichlorhydrin Nitrate, $\text{C}^2\text{H}^3\text{Cl}^2\text{NO}_3$, is formed as an intermediate product of the action of nitric acid on L. Henry's dichlorhydrin, the final product being dichloropropionic acid (p. 876). It is a colourless liquid having a peculiar aromatic odour and sweet taste. Sp. gr. 1.3 at 7° ; boiling point 180° (L. Henry, *Deut. Chem. Ges. Ber.* vii. 409).

Ethyl Nitrate, $\text{C}^2\text{H}^5\text{NO}_3$.—G. Bertoni (*Gazz. chim. ital.* 1876, 406) prepares this ether by a modification of the ordinary process, whereby large quantities of it may be obtained in a short time. 150 c.c. nitric acid of sp. gr. 1.36 are poured upon 10 grams of urea contained in a retort—the acid having been previously heated with a small quantity of urea—and heat is applied till the whole of the urea is dissolved. 150 c.c. alcohol of 92 per cent. are then poured to the bottom of the retort through a long-necked funnel, so that the two liquids may immediately mix. The liquid is then distilled till the greater part has passed over, and the residue is again treated with 150 c.c. of alcohol and acid and distilled. After this second distillation, a further quantity of ethyl nitrate may be obtained by adding 50 c.c. of alcohol and acid, and distilling a third time.

NITROGLYCERIN. See GLYCERIN (p. 875). A comprehensive memoir on this compound has been published by A. Brull in the *Bulletin de la Société d'Encouragement*, 1877, iv. 493, 562.

NITROLIC ACIDS. See NITROPARAFFINS, under PARAFFINS.

NITROMETHYLBENZOPHENONE, $\text{C}^1\text{H}^{11}(\text{NO}_2)\text{O}$. See vii. 861; also TOLYL-PHENYL KETONES in this volume.

NITROPARAFFINS. See PARAFFINS.

NITROPHOSPHENYLIC ACID. See PHOSPHENYLIC ACID.

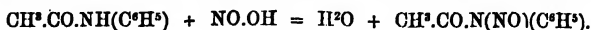
NITROPROPIOPHENONE, $\text{C}^6\text{H}^4(\text{NO}_2)\text{CO} \cdot \text{C}^2\text{H}^3$. See KETONES (p. 1152).

NITROPRUSSIDES. It is commonly stated that these compounds are not attacked by chlorine. According to E. W. Davy, however (*Chem. News*, xxxviii. 105), chlorine does act on them, very slowly under ordinary circumstances, but much more quickly in bright sunshine, under the influence of which it soon decomposes them completely. *Sodium nitroprusside* thus treated is resolved into ferric chloride, sodium chloride, hydrochloric acid, and the compound $\text{C}^{\text{N}}\text{Cl}^4$, known as chlorocyanic oil. The nitroprussides of *potassium, barium, calcium, zinc, iron, manganese, and silver* are attacked in a similar manner, the *copper salt* being the only one which resists the combined action of chlorine and light. Heat, like light, appears to aid the decomposing action.

Sodium Nitroprusside has, according to Clarko (*Sill. Am. J.* [3], xiv. 281), a sp. gr. of 1.6896 at 25° . Schröder found 1.710 and 1.716.

According to Filhol (*N. Rep. Pharm.* xxiv. 242), a solution of this salt, mixed with hydrogen sulphide, is an extremely delicate test for the alkalinity of a liquid, producing a blue-violet colour, not only with free alkalis, but also with alkaline carbonates, borates, phosphates and silicates.

NITROSACETANILIDE, or *Acetylphenylnitrosamine*, $\text{CH}^3\text{CO} \cdot \text{N}(\text{NO})(\text{C}^6\text{H}^5)$, is formed by the action of nitrous acid on acetanilide dissolved in cooled glacial acetic acid:

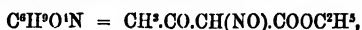


The reaction, which takes place very nearly in the proportions thus indicated, is com-

plete when the solution exhibits a green colour arising from excess of nitrous acid. The nitrosacetanilide may be purified by solution in glacial acetic acid and precipitation by water. It is a very unstable compound, decomposing, when kept, with evolution of nitrous acid; when boiled with water, it melts and is converted into a greasy mass. It dissolves readily in glacial acetic acid, and the solution, when left to evaporate, deposits crystals which change into a black substance. By quick evaporation of the ethereal solution, slender needles are obtained. With phenol and sulphuric acid, nitrosacetanilide gives Liebermann's colour reactions (vii. 901). It melts at 40° – 41° , and detonates at a higher temperature. Its dust excites sneezing. By reducing agents it is reconverted into acetanilide (O. Fischer, *Ber.* ix. 463; comp. W. Heintz, *ibid.* 1573).

Nitrosacetoparatoluide, $\text{CH}^3\text{C}^6\text{H}^4\text{N}(\text{NO})\text{C}^2\text{H}^3\text{O}$, obtained in like manner, melts with decomposition at 80° , and detonates at a higher temperature (Fischer, *ibid.* x. 959).

NITROSACETOACETATE (ETHYLIC),



formed by the action of nitrous acid upon ethyl acetoacetate, was originally obtained as a heavy yellowish oil, which did not solidify at -25° , but after it had remained liquid for some months, a small quantity of it suddenly crystallised, and, by introducing the crystals thus formed into the liquid acid, a large quantity of it was obtained in the crystalline state. The crystals are hard colourless shining prisms, melting at 52° – 54° to a transparent liquid which is completely decomposed by distillation (Meyer a. Züblin, *Ber.* xi. 320).

NITROSAMARINE, $\text{C}^{21}\text{H}^{17}(\text{NO})\text{N}^2$. See AMARINE (p. 70).

NITROSAUSTRALENE. See NITROSOTERPENES (*infra*).

NITROSETHYLANILINE, $\text{C}^6\text{H}^5\text{N}(\text{NO})(\text{C}^2\text{H}^5)$. See ETHYLANILINE⁴, under BENZENES, AMIDO- (p. 206).

NITROSETHYLPHENYLSEMICARBAZIDE,



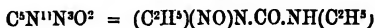
See HYDRAZINES (p. 1055).

NITROSINDOL, $\text{C}^{16}\text{H}^{12}(\text{NO})\text{N}^2$. See INDOLE (p. 1090).

NITROSOCHLORIDHESPERIDENE. See NITROSOTERPENES.

NITROSODIETHYLANILINE, $\text{C}^6\text{H}^4(\text{NO}).\text{N}(\text{C}^2\text{H}^5)_2$, obtained by the action of amyl nitrite, alcohol, and hydrochloric acid on diethylaniline, crystallises in large prisms melting at 84° , and decomposes at a higher temperature. It dissolves in alcohol and in ether, less easily in water. Its salts are yellow, and dissolve readily in water and in alcohol. It yields addition-products (A. Kopp, *Ber.* viii. 621).

NITROSODIETHYL-CARBAMIDE,



(E. Fischer, *Ber.* ix. 111). This compound, which v. Zotta obtained by treating diethyl-carbamide with alkaline nitrites (*Liebig's Annalen*, clxxix. 101), is more readily obtained in the pure state by passing nitrous acid in excess into an ethereal solution of the carbamide. On leaving the ether to evaporate at a very low temperature, washing the residual oil with water, redissolving it in ether, drying the solution with calcium chloride, and again leaving it to evaporate, an oily residue is left, from which, after long standing in the cold and in a vacuum, nitrosodiethyl-carbamide is deposited in well-defined transparent plates melting at 5° . It is indifferent to acids and alkalis. In contact with phenol and sulphuric acid, it produces Liebermann's dyes (p. 697). By reduction with zinc-dust and acetic acid it is converted into diethylhydrazine-carbamide, $(\text{C}^2\text{H}^5)(\text{NH}^2)\text{N.CO.NH}(\text{C}^2\text{H}^5)$. The reduction, which should take place at a temperature not exceeding 20° – 25° , is complete when the liquid no longer becomes turbid on addition of hydrochloric acid and water. On evaporating the filtered solution, mixing it with potash-ley in a cooled vessel, agitating the liquid several times with ether, and evaporating the ethereal extract, diethylhydrazine-carbamide remains in the form of a colourless syrup, easily soluble in water, alcohol, and ether, not altered by boiling with water, decomposing without carbonisation when strongly heated. It has an alkaline reaction, and when dissolved in potash reduces Fehling's solution and platinic chloride. By alkalis, and more easily by heating it in a sealed tube on the water-bath with 3 or 4 pts. hydrochloric acid of

sp. gr. 1.19, it is resolved, with assumption of water, into carbon dioxide, ethylamine, and ethyl-hydrazine (p. 1061). The *hydrochloride*, $C^2H^4N^2O.HCl$, obtained by acidulating its alcoholic solution with fuming hydrochloric acid, and adding ether, crystallises in white slender needles easily soluble in water and in alcohol, less easily in strong hydrochloric acid, and decomposing when heated. The *platinochloride*, $(C^2H^4N^2OCl)^2PtCl_4$, crystallises in fine yellow needles.

NITROSODIMETHYLAMINE, $C^2H^4N^2O = (CH^3)^2N-N=O$, also called *Dimethylnitrosamine* and *Nitrosodimethylamine*. The hydrochloride of this base is formed by heating a concentrated, acidulated, aqueous solution of dimethylamine hydrochloride with potassium nitrite to $60^\circ-70^\circ$. It is a yellow oil having a peculiar pungent odour, and reduced by zinc-dust and acetic acid to hydrochloride of dimethylhydrazine, $(CH^3)^2N-NH^2$ (p. 1063), (E. Fischer, *Ber.* viii. 1587).

NITROSODIMETHYLANILINE, $C^6H^4(NO).N(CH^3)^2$, also called *Dimethylnitrosaniline*. The preparation of the hydrochloride of this base by the action of nitrous acid on dimethylaniline hydrochloride, as practised by Baeyer & Caro, has already been described (p. 205). C. Schranbe (*Ber.* ix. 716) adds 75 pts. amyl nitrite cooled to 0° to an ice-cold mixture of 50 pts. dimethylaniline, 100 strong hydrochloric acid and 600 of a mixture of 1 vol. hydrochloric acid and 2 vols. alcohol.

Nitrosodimethylaniline melts at 85° . Its salts, formed by adding dilute aqueous or ethereal solutions of the respective acids to an ethereal solution of the base, crystallise well for the most part. Especially characteristic is the *neutral oxalate*, which, when recrystallised from wood-spirit, forms brown-red monoclinic crystals containing 2 mols. water.

Addition-products, in large splendid steel-blue crystals, are formed on heating a solution of this nitroso-base in alcohol or benzene with aniline or paratoluidine. The addition-product of *dimethylaniline* and nitrosodimethylaniline crystallises from benzene in dark-green shining crystals which effloresce quickly on exposure to the air. The *phenol-addition-product*, formed by mixing 2 mols. nitrosodimethylaniline and 1 mol. phenol, with addition of water, crystallises in brown slender needles which give off all their phenol at 70° . Nitrosodimethylaniline also unites with *silver nitrate*, forming an addition-product which may be recrystallised from water at 25° , and then forms small dark-blue shining crystals, violet by transmitted light.

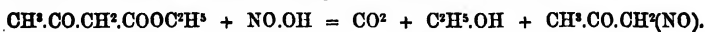
Nitrosodimethylaniline is reduced by *tin* and *hydrochloric acid* to phenylene-dimethyldiamine, $N^2H^2(C^6H^4)(CH^3)^2$ (see PHENYLENE-DIAMINES). By *potassium ferricyanide*, or better by *permanganate*, it is oxidised to nitrodimeethylaniline, which is a base forming large sulphur-yellow crystals melting at 169° . *Nitric acid* oxidises nitrosodimethylaniline with great violence; nevertheless, it is possible, by careful treatment with dilute nitric acid, to carry the action as far as the formation of dinitrodimeethylaniline, which forms large yellow crystals melting at 73.5° , and may be recrystallised from ether-alcohol. With *aniline acetate*, nitrosodimethylaniline forms azophenine, $C^6H^2N^2O$, together with other products (Kimich, p. 138).

NITROSOFORMANILIDE, $C^6H^3.N(NO)(CHO)$, prepared by the action of nitrous acid on formanilide, melts at 39° (Fischer, *Ber.* x. 959).

NITROSOFURFURINE, $C^4H^4(NO)N^2O$. See FURFURINE (p. 837).

NITROSOGUANIDINE, $CH^4(NO)N^2$. See GUANIDINE (p. 904).

NITROSO-KETONES (V. Meyer & J. Zübelin, *Ber.* xi. 320, 692). 1. *Methyl-nitrosomethylketone* or *Nitrosacetone*, $C^3H^5NO^2 = CH^3.CO.CH^2(NO)$, is formed by the action of nitrous acid on the ethylic ether of acetoacetic acid:

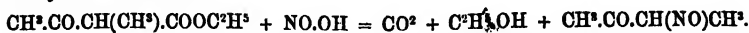


To prepare it, ethyl acetoacetate (1 mol.) is added by successive portions to a solution of alcoholic potash (1 mol.); the mixture is diluted with water; a solution of potassium nitrite (1 mol.) is added; the liquid is acidulated with dilute sulphuric acid and again supersaturated with potash; the unattacked ethyl acetoacetate is dissolved out by ether; the alkaline liquid left at rest for three or four days, then again acidulated with sulphuric acid, and several times exhausted with ether; and the greater part of the ether is removed by distillation, the remainder by leaving the solution for several days over sulphuric acid. The product thus obtained is a light yellow oil, which may be made to crystallise by spreading it out on a number of flat-bottomed dishes, and leaving these over sulphuric acid.

Nitrosacetone consists of silvery plates or prisms melting at 65° , easily soluble in ether, and in cold or hot water. It passes over readily with steam, but cannot be distilled alone without decomposition. It has acid properties, and its alkaline solution is intensely yellow; it gives a yellow solution with phenol and sulphuric acid.

2. *Methyl-nitrosoethyl Ketone* or *Nitrosomethylacetone*, $C^4H^7NO^2 =$

$\text{CH}^3\text{CO.CH(No)CH}^3$, is formed by the action of nitrous acid on the ethylic ether of methylacetoacetic acid :



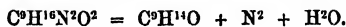
It crystallises from water in pearly scales, and from its solutions in ether, alcohol, and chloroform in colourless prisms, which melt at 74° . It boils without decomposition at 185° ; and has a vapour-density of 3.51, exactly coinciding with that required by the formula $\text{C}^4\text{H}^7\text{NO}^2$.

3. *Methylnitrosopropyl Ketone* or *Nitroethylacetone*, $\text{C}^4\text{H}^7\text{NO}^2 = \text{CH}^3\text{CO.CH(No)(C}^2\text{H}^5\text{)}$, obtained like the preceding, forms colourless crystals easily soluble in alcohol, ether, and chloroform, melting at 53° – 55° .

Both these nitrosoketones give deep red solutions with phenol and sulphuric acid, and a fiery saffranine-red colour when they are dissolved in aniline, and glacial acetic acid is added to the solution.

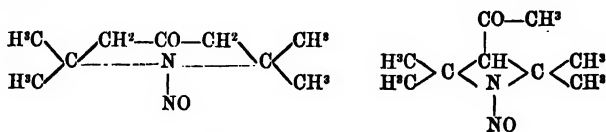
NITROSOTRIACETONAMINE, $\text{C}^6\text{H}^{16}\text{N}^2\text{O}^2 = \text{C}^6\text{H}^{16}(\text{NO})\text{NO}$ (Hantzsch, *Liebigs Annalen*, clxxxv. 1; clxxxvii. 233). This compound is formed on mixing the neutral solutions of triacetoneamine hydrochloride and potassium nitrite, and separates after a while in long faintly yellowish crystals, a further quantity of which may be obtained by gently warming the decanted liquid, and then leaving it to cool. Nitrosotriacetoneamine cannot be recrystallised from hot water without loss, as it volatilises with the vapour; but it may be purified by dissolving it in very slightly warmed alcohol, and precipitating it at 50° by gradual addition of water.

Nitrosotriacetoneamine has a specific gravity of 1.14; melts at 72° – 73° ; sublimes, though very slowly, below its melting-point; dissolves readily in alcohol and ether, and crystallises therefrom in long needles; is neutral to litmus-paper. By the action of potash, or by prolonged boiling of its aqueous solution, it is resolved into nitrogen, water, and phorone :



When nitrosotriacetoneamine is heated with hydrochloric or strong sulphuric acid, the greater part of it is converted into triacetoneamine; but at the same time four other bodies are formed, viz., two bases—one having the composition $\text{C}^6\text{H}^{16}\text{N}^2\text{O}$ —whose hydrochlorides are sparingly soluble in water, and two substances which exhibit the characters of amido-acids. Nitrous acid does not reduce nitrosotriacetoneamine to amidonitrosamine.

The constitution of nitrosotriacetoneamine may be represented by one of the following formulæ :



NITROSYL-COMPOUNDS. The *Sulphate*, H(No)SO^4 , or $\text{SO}_2\left\{\begin{smallmatrix} \text{OH} \\ \text{ONO} \end{smallmatrix}\right.$ identical with the 'lead-chamber crystals,' is easily prepared by saturating cold strong sulphuric acid with nitrogen trioxide, or by passing sulphur dioxide into nitric acid; most advantageously however by burning a mixture of 1 pt. sulphur with 2.5 to 3 pts. potassium nitrate in moist air (Girard a. Pabst, *Bull. Soc. Chim.* [2], xxx. 531). Tilden prepares it by passing the gases evolved from aqua regia and dried by calcium chloride into cold strong sulphuric acid. It forms long thin prismatic crystals melting at 85° – 87° . When gently heated with dried chloride or bromide of sodium, it yields the corresponding chloride or bromide, NOCl or NOBr ; and with potassium nitrate in like manner it yields nitrogen tetroxide, N^2O^4 , which may therefore be regarded as nitrosyl nitrate, NO.NO^3 (Girard a. Pabst). Compare p. 410.

Nitrosyl Chloride, NOCl , is an orange-yellow gas which condenses in a freezing mixture to a deep yellow liquid boiling at -8° . The density of its vapour was found to be 2.33–2.29 at 10° (air=1), or 33.5–33.0 ($\text{H}=1$); calc. 32.75. The *dichloride*, NOCl^2 , said by Gay-Lussac to be formed, together with other products, by the distillation of aqua regia, was probably a solution of the monochloride in chlorine gas. The reaction between hydrochloric and nitric acids may be represented by the equation



(Tilden, *Chem. Soc. J.* xxviii. 630).

Nitrosyl Bromides.—The monobromide, NOBr, prepared like the chloride by distilling nitrosyl sulphate with sodium bromide, is described by Girard a. Pabst as an easily decomposable liquid boiling at 19°. According to Landolt, on the other hand, who prepared it by passing nitrogen dioxide into bromine cooled below -4°, it is a blackish-brown liquid which begins to boil and give off brown-red vapours at -2°, sinks unaltered in very cold water, begins to form bubbles of nitrogen dioxide if heated therein to 14°, and if then stirred with a sharp-edged glass rod or a wire, gives off torrents of gas, being decomposed in the manner represented by the equation



The tribromide, NOBr₃, is formed by decomposition of the monobromide, and remains as a dark brownish-red liquid when the temperature is allowed to rise to about 23°. It is also formed by saturating bromine with nitrogen dioxide at ordinary temperatures, and Muir has shown (*Chem. Soc. J.* xxviii. 844) that the compound thus formed has the same composition whether the absorption takes place under the ordinary atmospheric pressure or at any lower pressures down to 250 mm. It has a specific gravity of 2.628 at 22.6°, volatilises almost without decomposition when quickly heated, but is resolved by slow distillation into nitrogen dioxide and bromine (Landolt, *loc. cit.*)

NITROTOLYL-PHENYL KETONES. The mononitro-derivative, C¹⁴H¹¹(NO²)O, (*Nitromethylbenzophenone*), obtained by the action of fuming nitric acid on solid paratolyl-phenyl ketone (p. 1154), is identical with that which Milne obtained (*Ber.* v. 693) by heating benzyl-toluene with nitric acid of sp. gr. 1.4. It crystallises from hot alcohol in broad shining laminae or in needles, melts at 126°-127°, and sublimes easily in shining laminae; dissolves readily in chloroform, benzene, and hot acetic acid. When its solution in glacial acetic acid is boiled with chromic acid, benzoic and nitrobenzoic acids are produced, the latter melting at 140°, and yielding a barium salt which crystallises with 4H₂O. The greater part of the nitro-ketone is however completely burnt, and it has not been found possible to obtain the first product of the oxidation, viz., mononitrobenzoylbenzoic acid (Plascuda a. Zincke, *Ber.* vii. 982). By tin and hydrochloric acid, the nitroketone is converted into the corresponding amido-compound, which is precipitated from its solution in hydrochloric acid by soda-ley, in the form of a loose white powder. It dissolves readily in alcohol and ether, and forms with acids uncrystallisable salts which dry up to gummy masses (Milne).

Dinitro-tolyl-phenyl Ketone, C¹⁴H¹⁰(NO²)₂O, is formed by boiling dinitrobenzyl-toluene (vii. 183) for a considerable time with nitric acid of sp. gr. 1.4, or by heating its solution in glacial acetic acid with chromic acid. It crystallises from acetic acid in thick yellowish needles, from alcohol in silky laminae; melts at 126°-127°; decomposes without subliming at a higher temperature; and dissolves with moderate facility in benzene and in chloroform, less easily in ether. By oxidation it is converted into paranitrobenzoic acid and dinitrobenzoylbenzoic acid, C¹⁴H⁹(NO²)₂O₃, melting at 211°-212° (Plascuda a. Zincke).

Trinitro-tolyl-phenyl Ketone, C¹⁴H⁹(NO²)₃O, obtained by adding solid tolyl-phenyl ketone, or its mono- or dinitro-derivative, to a mixture of nitric and sulphuric acids, crystallises from acetic acid or alcohol in small, yellowish, well-defined prisms; melts at 165°, and decomposes at a higher temperature without subliming (Plascuda a. Zincke).

NOMENCLATURE. Suggestions with regard to Chemical Nomenclature, chiefly with the view of securing uniformity of termination in the names assigned to different classes of compounds, have lately been drawn up by the Council of the Chemical Society, and published in the Journal of that Society (1879, vol. xxxv. pp. 277-280).

The terminations recommended are for the most part the same as those which have been used in this Dictionary (see vol. iv. p. 133); but attention may be especially directed to the recommendation respecting the use of the terminal 'ol' for all hydroxyl-derivatives of hydrocarbons, in other words for all compounds of alcoholic character, and its absolute restriction thereto. Thus glycerin, erythrite, mannite, hydroquinone, resorcin, pyrocatechin, saligenin, are in future to be called glycerol, erythritol, mannitol, quinol, resorcinol, catechol, saligenol; and, on the other hand, the ethers of the phenols, e.g. C⁶H⁵.OCH₃, C⁶H⁵.OC²H₅, &c., hitherto called anisol, phenetol, &c., are to be designated as anisoil, phenetoil, &c.; and certain aldehydes, hitherto denoted by names ending in *ol*, are to be designated, like aldehydes in general, e.g. the so-called furfural as furfuraldehyde or furfural. Other compounds which are

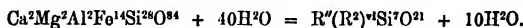
not alcohols, but have hitherto been known by names ending in *ol*, may be represented by names ending in *ole*—*e.g.* indole instead of indol. The hydrocarbon C^8H^8 and its homologues, sometimes called benzol, toluol, &c., are to be called benzene, toluene, &c.

Another point deserving of special remark is the use of the terminations *ine* and *in*, the former for organic bases, ethylamine, aniline, toluidine, quinine, morphine, &c., the latter for certain neutral compounds, viz. glycerides, glucosides, bitter principles, and proteids, *e.g.* palmitin, amygdalin, albumin, casein,* &c.

NONTRONITE. A mineral resembling nontronite (iv. 134) has been found by A. Schrauf (*Jahrb. f. Min.* 1877, 255) in the Wenzel shaft at Mugrau in Bohemia, forming layers of lenticular nodules alternating with graphite. Under the microscope it appears to be made up of irregular, semitransparent laminæ, exhibiting slight double refraction. The amount of water varies considerably. The following analyses relate to material well dried in the air; the powder, after drying over sulphuric acid, gave 13.59 per cent. water; after exposure to moist air, 22.02 per cent.

SiO ²	Fe ² O ³	Al ² O ³	CaO	MgO	H ² O
43.98	27.50	4.16	2.97	1.77	19.62 = 100
42.93	28.01	3.19	3.35	2.84	18.32 = 99.54

These analyses may be represented by the formula:



NONYLACETYLENE, or *Rutylidene*, $C^{11}H^{20} = (C^8H^{10})C \equiv CH$, is formed from the methyl-nonyl-ketone which is the chief constituent of rue-oil (vii. 808), by treating this ketone with PCl^5 , and abstracting 2 mols. HCl from the resulting chloride, $CH^3.CCl^2.C^8H^{10}$, by the action of potash. It is an oily liquid, boiling at 215° – 220° , and forming with ammoniacal silver-solution a white precipitate, $C^{11}H^{10}Ag$, with copper-solution a yellow-brown precipitate (Bruylants, *Ber.* viii. 406, 410).

NORTON'S SALT, $PLCl^4OH^2$. See PLATINUM CHLORIDES.

NOSEAN-ANDESITE. See ISENITE (p. 1125).

NOSEAN-PHONOLITE. A specimen of this rock from Hohentwiel in Högau has been analysed by J. Bernath (*Jahrb. f. Min.* 1877, 740):

A. Fresh rock; 55.9 per cent. soluble, 44.1 per cent. insoluble. B. Weathered; 39 per cent. soluble, 61 per cent. insoluble.

SiO ²	Al ² O ³	Na ² O	K ² O	CaO	H ² O	Fe ² O ³	FeO	MgO
55.214	21.782	10.637	3.475	2.097	2.069	2.061	2.006	0.127 = 99.468
55.842	19.871	8.058	6.231	—	3.874	2.583	1.549	1.810 = 99.818

Moreover, in A, 0.546 per cent. SO^2 , 0.074 Cl. In both, traces of manganese, titanium, and lithium. Sp. gr. of A = 2.64; of B, 2.41.

NOVACULITE. An analysis, by C. E. Wait, of this material, also called *Ouachita Whetstone*, from Hot Springs, Arkansas, has been published by J. W. Mallet (*Chem. News*, xxviii. 272):

SiO ²	Al ² O ³	MgO	Na ² O	Sp. gr.
99.635†	0.113	0.087	0.165 = 100	2.649

The mass, of which a small proportion is soluble in caustic soda, is essentially a crypto-crystalline quartz containing, in addition to the above constituents, traces of potassium and iron.

NUCIN. This substance, also called *Juglone*, which Vogel a. Reischauer obtained from the green shells of walnuts (iv. 143), has been analysed, together with the copper-compound obtained by precipitating its alcoholic solution with cupric acetate, by Reischauer (*Deut. Chem. Ges. Ber.* x. 1542), who finds it to have the composition $C^{26}H^{12}O^{10}$.

NUCITE. A variety of glucose, obtained from the leaves of the nut-tree.

NUCLEIN (iv. 143; vii. 862). This substance has been found in the human brain to the amount of 1.4 pts. in a thousand (Geoghegan, *Zeitschr. physiol. Chem.* i. 330); in the spermatie chords of the salmon, to the amount of 48.7 per cent., united with an organic base called *protamine* (Miescher, *Ber.* vii. 376); and in the casein of cows' milk (Lubavin, *ibid.* x. 917). Puro nuclein from this last mentioned

* This distinction was suggested many years ago, by Dr. Hofmann, and has been uniformly observed in this Dictionary; but many writers unfortunately neglect it, and use the two terminations indiscriminately.

† Determined by difference.

source may be obtained by digesting commercial casein (previously freed from fat in an extraction-apparatus) with artificial gastric juice at 40°; washing the undissolved residue with hot and cold water; then dissolving it in a 1 per cent. solution of sodium carbonate; precipitating the filtered solution with weak hydrochloric acid; and washing the precipitate with water, alcohol, and ether in succession. That nuclein is not a phosphate of casein is inferred by Lubavin from the following facts: When a solution of nuclein in excess of sodium carbonate is dialysed, the diffuseate does not exhibit a trace of phosphoric acid till decomposition has set in. Nuclein cannot be prepared synthetically from casein and sodium phosphate; from a solution of casein in that salt, magnesia-mixture throws down the whole of the phosphoric acid, whereas the phosphoric acid of nuclein is not precipitated by similar treatment. When a solution of casein in aqueous sodium phosphate is mixed with 1 per cent. hydrochloric acid, the precipitate formed by the first drops of acid disappears on further addition, and the resulting solution gives a precipitate when cautiously neutralised with ammonia or mixed with solution of common salt or sal-ammoniac. Lubavin regards nuclein as a mixture of at least two distinct compounds, inasmuch as the partial precipitates obtained from its solution in sodium carbonate by successive addition of equal amounts of hydrochloric acid differ from one another in composition, and the precipitates formed by successive addition of equal amounts of hydrochloric acid, likewise differ in quantity. The isolation of the chemically distinct individuals existing in nuclein has not yet been accomplished. Nuclein has a marked acid character; it reddens litmus and decomposes carbonate and even acetate of sodium. The solution of nuclein in sodium acetate gives precipitates with zinc, copper, and lead salts; the lead precipitate is white, granular, and easy to wash. The precipitation of nuclein by lead acetate is not complete, and fractional precipitation yields precipitates containing different quantities of lead (Lubavin).

Digestibility.—From experiments by A. Bókay (*Zeitschr. physiol. Chem.* i. 157), it appears that nuclein is not attacked by any of the digestive ferments, and that it is probably a constant constituent of fecal matters, since it is present in nearly all kinds of food.

NUX VOMICA. According to C. Bullock (*Pharm J. Trans.* [3], v. 326), the oil of *Nux vomica*, separated in the preparation of the extract, contains both strychnine and brucine.

O.

OBSIDIAN. Obsidian from Antisana has been found by G. vom Rath (*Zeitschr. geol. Ges.* xxvii. 295) to contain:

SiO ²	Al ² O ³	Fe ² O ³	CaO	$\overbrace{K^2O \ Na^2O}^{\quad}$	H ² O	Sp. gr.
77.76	13.14	1.47	0.63	7.00	0.24 = 100.24	2.320 at 10°

An analysis by J. A. Cabell of the outer crust of a mass of obsidian from Lipari, which had been exposed to the action of volcanic vapours, has been published by J. W. Mallet (*Chem. News*, xxviii. 272):

SiO ²	Al ² O ³	¹ / ₂ CaO	Fe ² O ³	Fe ² Cl ³	H ² O*	H ² O†	Sp. gr.
93.46	0.37	0.74	0.37	0.15	4.55	0.08 = 99.72	2.062

Tumefaction of Obsidian by Heat.—Obsidian when strongly heated swells up suddenly, and is converted into pumice. This result is attributed by Bousisingault a. Damour (*Compt. rend.* lxxvi. 1158; *Ann. Chim. Phys.* [4], xxix. 543; *Chem. Soc. J.* xxvi. 856) to a sudden disengagement of vapours of water and hydrochloric acid, the latter resulting from the action of the silicates on the chlorides contained in the mineral. The following are some of the analytical data on which this conclusion is founded:

A. Loss on ignition. B. Direct estimation of the water. C. Of the hydrochloric acid. D. Amount of chlorine reckoned as HCl. E. After fusion. The whole of the values are calculated in percentages of the substance experimented on.

* Above 100°.

† At 100°.

	A	B	C	D	E
Volcano of Paracé (Pasambro, Columbia)	0.556	—	—	—	—
Mexico	0.211	—	—	—	—
Mexico	0.630	—	—	—	—
California	0.104	—	—	—	—
Ecuador	0.118	—	—	—	—
Caucasus	0.168	—	—	—	—
Cerro de las Navajas (Mexico)	0.330	0.277	0.104	0.2550	0.0904
Iceland	0.450	0.394	0.0575	0.1936	0.0968
Mexico	0.690	0.636	0.112	0.2497	0.0968
Ecuador	0.235	0.121	0.0186	0.0870	0.0662
Lipari	0.780	0.4715	0.144	0.2750	0.1327

OCTAMINE COBALT-COMPOUNDS. See COBALT (p. 546).

OCTANE, C^8H^{18} . The octane obtained by the action of zinc and hydrochloric acid on methyl-hexyl-carbinyl iodide, $(CH^3)_2CHI(C^6H^{13})$ (from castor-oil alcohol, vi. 877), has the same boiling point (124°) and sp. gr. (0.7083 at 12.5°) as that which is produced by the action of sodium on normal butyl iodide (vii. 867); it is, therefore, normal octane, $CH^3(CH^2)^6CH^3$; and this conclusion is in accordance with the fact that the methyl-hexyl carbinol from castor-oil is converted by oxidation into normal caproic acid (Schorlemmer, *Chem. Soc. J.* [2], xii. 1029).

An octane, perhaps identical with the preceding, is obtained, together with other paraffins, among the products of the distillation of fatty acids with overheated steam (Cahours a. Demarçay, *Compt. rend.* lxxx. 1568).

Di-isobutyl, $(CH^3)_2CH.CH^2.CH^2.CH(CH^3)^2$. This is the octane which Kolbe obtained by the electrolysis of potassium valerate, and Wurtz by the action of potassium or sodium on isobutyl iodide (v. 731). Schorlemmer (*Proc. Roy. Soc.* 1876, 34) obtained it by the action of sodium on a mixture of the iodides of isopropyl and isopentyl (amyl); and it has lately been further investigated by W. Carleton-Williams (*Chem. Soc. J.* 1877, xxxi. 541; 1879, xxxv. 125), who prepares it by the action of sodium on isobutyl bromide, and purifies it by leaving it in contact for several hours with strong sulphuric acid, then washing it with water, leaving it over solid caustic potash for two or three days, and finally subjecting it to fractional distillation.

Pure di-isobutyl thus obtained boils, under a pressure of 745 mm. (reduced to 0°), at 108° – 108.3° (mercury-column wholly in the vapour), remains liquid at -17° , and exhibits the following densities at different temperatures:

t.	Sp. gr.	t.	Sp. gr.
0°	0.7091	30°	0.686
0°	0.7085	40°	0.677
10°	0.7015	50°	0.669
20°	0.6931	100°	0.626

These results agree closely with those obtained by Kopp (v. 731). The vapour-density, determined by Victor-Meyer's process (*Ber.* x. 2068), was found in two experiments to be 57.64 and 58.51; calc. 57 ($H = 1$).

An examination of the refractive power gave the following results:

	Potassium (red line)	Lithium	Sodium	Thallium	Strontium (blue line)
Refractive indices at $16^\circ = \mu$	1.3901	1.3917	1.3943	1.396	1.4008
Refractive energy $\frac{\mu-1}{d}$	0.5591	0.5618	0.5655	0.568	0.5748
$d = 0.6972$ at 16°					
Refraction equivalent, $P \frac{\mu-1}{d}$ (vi. 783.)	63.78	64.04	64.47	64.75	65.55

On the assumption that $C = 5$ and $H = 1.3$, the calculated refractive equivalent for di-isobutyl is 63.4.

Di-isobutyl has no action on polarised light.

On the action of *chlorine* on di-isobutyl, see p. 1425.

OCTOBROMETHYL OXIDE, $(C^2HBr^2)^2O$, is formed, together with other products, by heating ethylidene oxychloride (p. 757) with bromine for ten hours at 100° , 150° – 190° , and 190° – 210° , till it begins to carbonise. The syrupy product, when redistilled, separates into three portions, the first of which (b. p. 130° – 190°) contains the octo-brominated ether. This compound is a thickish liquid having an odour of perspiration, fuming very slightly in the air, insoluble in water, but decomposing when left in contact therewith at ordinary temperatures, more quickly on boiling (F. Kessel, *Ber.* x. 1667).

OCTOIC ACIDS, $C^8H^{16}O_2 = C^7H^{15}.COOH$. (1). The identity of the iso-octoic acid, $(CH^3)^2CH.(CH^2)^4.COOH$, obtained by oxidation of isoprimary octyl alcohol, with caprylic acid prepared by saponification of cocoa-nut oil, has been already noticed (p. 379).

(2). Another iso-octoic acid, $(CH^3)^2CH.CH^2.CH^2.CH \begin{smallmatrix} CH^3 \\ \diagup \\ COOH \end{smallmatrix}$, formed by oxidising the corresponding alcohol from di-isobutyl with chromic acid mixture, is an oily liquid, which boils at 218° – 220° under 767 mm. pressure (reduced), and does not solidify at -17° . It is soluble in alcohol and in ether, and sparingly soluble in water, 100 c.c. of water at 15° dissolving 0.15 gram of the acid. At the ordinary temperatures it has an unpleasant odour, which becomes much more powerful at higher temperatures, when it somewhat resembles that of rotten cheese. The sp. gr. of the acid compared with water at 4° is:

At 0°	0.926	40°	0.893
„ 20°	0.911	50°	0.885
„ 30°	0.903	100°	0.846

The *sodium salt*, prepared by neutralisation, remains, after evaporation over sulphuric acid, as a deliquescent gummy mass, which begins to crystallise after standing for several days over sulphuric acid in a vacuum. The *potassium salt* is a semi-crystalline deliquescent mass. The *silver salt*, $C^8H^{15}AgO_2$, is a white curdy precipitate, slightly soluble in boiling water, and separating on cooling in silky threads or small tooth-shaped crystals. The *calcium salt*, $(C^8H^{15}O_2)_2Ca + 11H_2O$, prepared by neutralising the acid with milk of lime, may be obtained by spontaneous evaporation in radiate groups of well-formed crystalline plates. It is more soluble in cold than in warm water, a solution saturated at 15° becoming turbid at 37° ; the density of the precipitate increases with the temperature, and the salt redissolves on cooling. The *barium salt*, prepared by boiling barium carbonate in the acid, is uncrystallisable and remains as an amorphous pellicle on leaving the solution to evaporate in a vacuum. The *strontium salt* may be prepared by neutralisation, and is precipitated on mixing the concentrated solutions of strontium nitrate and potassium iso-octoate. It dissolves freely in absolute alcohol, and is deposited from the alcoholic solution in transparent six-sided plates, which appear to belong to the monoclinic system, and to consist of a combination of the basal terminal plane with the clinodiagonal and orthodiagonal domes. The salt is slightly less soluble in hot than in cold water, a solution saturated at the ordinary temperature becoming slightly turbid when heated. From an aqueous solution it is deposited in transparent needle-shaped crystals, which effloresce and grow opaque on exposure to the air. The *magnesium salt*, $(C^8H^{15}O_2)_2Mg + 2H_2O$, prepared by neutralisation, is a transparent, deliquescent, non-crystalline mass, which slowly becomes opaque and crystalline when left in a vacuum over sulphuric acid. The *zinc-salt* is a white pearly mass, which is decomposed by water, but dissolves in the dilute acid.

The concentrated solution of the potassium salt produces in a solution of *mercuric chloride* a faint turbidity; with *mercuric nitrate* no precipitate; with *mercurous nitrate* a dense white precipitate, which is soluble in hot water and crystallises out again on cooling. *Lead acetate* and *manganese nitrate* form amorphous precipitates insoluble in water. *Cupric acetate* throws down a green precipitate, insoluble in water, but soluble in alcohol, forming a green solution, from which the copper salt is deposited in minute green plates, which are generally arranged together in pyramidal clusters (W. C. Williams, *Chem. Soc. J.* xxxi. 542; xxxv. 128).

Ethyl Isooctoate, $C^8H^{15}O_2.C^2H^5$, obtained by saturating an alcoholic solution of the acid with hydrochloric acid gas, is lighter than water, has a strong characteristic odour, and boils at about 175° . Vapour-density obs. 84.39; calc. 86.

Di-isobutyl Isooctoate, $C^8H^{15}O_2.C^4H^{11}$, formed in small quantity in the preparation of the acid by oxidation of the primary alcohol, is a colourless liquid, lighter than water, and boiling at 278° – 281° . It is slowly saponified by heating to 120° in sealed tubes with alcoholic potash (Williams).

(3). A third iso-octoic acid, probably having the constitution

$(\text{CH}^3)_2\text{CH}^2\text{CH}^1\text{COOH}$, is produced by oxidation of isodibutylene (p. 1130). It is a colourless oily liquid, smelling like trimethylacetic acid, and distilling with partial decomposition at $205^\circ\text{--}218^\circ$, the greater part passing over at about 215° (Butlerow).

OCTYL ALCOHOLS AND ETHERS. (1). Several derivatives of the iso-primary octyl alcohol, $(\text{CH}^3)_2\text{CH}(\text{CH}^2)_4(\text{CH}^2\text{OH})$, obtained by saponification of the volatile oil of *Heracleum sphondylium* and *H. giganteum* (vi. 878; vii. 868; viii. 1027), have been examined by W. Möslinger (*Deut. Chem. Ges. Ber.* ix. 998).

Isoctyl iodide, $\text{C}^8\text{H}^{17}\text{I}$, is best obtained by passing dry hydrogen iodide into octyl alcohol to saturation, and afterwards heating the liquid to 100° in closed vessels. The product contains 90 per cent. of pure octyl iodide boiling at $218^\circ\text{--}222^\circ$.

Isoctyl oxide, $(\text{C}^8\text{H}^{17})_2\text{O}$, was obtained by mixing equivalent quantities of sodium octylate (formed by the action of sodium on octyl alcohol) and isoctyl iodide, and heating the mixture to 100° for some time. It is a transparent oily-looking liquid, of specific gravity 0.805 at 17° , and boiling at $280^\circ\text{--}282^\circ$.

Isoctyl-ethyl ether, $\text{C}^8\text{H}^{17}\cdot\text{O}\cdot\text{C}^2\text{H}_5$, formed by heating together equivalent quantities of sodium octylate and ethyl iodide, is a colourless mobile liquid of agreeable odour, boiling at $182^\circ\text{--}184^\circ$. Sp. gr. 0.794 at 17° ; vapour-density, 78.79.

Isoctyl sulphide, $(\text{C}^8\text{H}^{17})_2\text{S}$.—Isoctyl chloride and potassium sulphide in alcoholic solution rapidly decompose each other when heated together. The isoctyl sulphide thus formed is a slightly yellow mobile liquid having a peculiar alliaceous odour and boiling with decomposition above 310° . Sp. gr. 0.8419 at 17° . It forms a crystalline compound with mercuric chloride.

Barium Isoctylsulphate, $(\text{C}^8\text{H}^{17}\text{SO}_4)_2\text{Ba}$, formed by carefully mixing equal weights of pure strong sulphuric acid and isoctyl alcohol, and after 24 hours neutralising the mixture with barium carbonate, crystallises in thin pearly laminae, which decompose at 100° , giving off isocytleno. The salt is very sparingly soluble in water.

Potassium Isoctylsulphate, obtained by decomposing the barium salt with potassium sulphate, is a white indistinctly crystalline mass, soapy to the touch, and easily soluble in water.

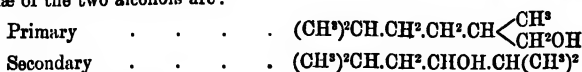
Isoctyl-phosphine, $\text{C}^8\text{H}^{17}\cdot\text{PH}_2$.—This body is formed when a mixture of phosphonium iodide, isoctyl iodide, and zinc oxide is heated to $160^\circ\text{--}180^\circ$ in sealed tubes. It is a transparent mobile liquid, highly refractive, and having the powerful, stupefying odour of all phosphines. Its boiling-point is $184^\circ\text{--}187^\circ$; sp. gr. 0.8209 at 17° . It absorbs oxygen from the air, but only slowly, the process going on for several days. The substance thereby formed is an acid intermediate between isoctyl-phosphine and the corresponding phosphinic acid, and hence may be termed *isoctyl-phosphinous acid*. Its silver salt is a white curdy precipitate, which is reduced by heat.

Isoctyl-phosphine in the pure state is very violently attacked by fuming nitric acid, but when it is diluted with glacial acetic acid, the action proceeds quietly, the product being isoctyl-phosphinic acid, a body which dissolves in hot glacial acetic acid and separates as the solution cools in a spermaceti-like mass. Isoctyl-phosphine is easily soluble in alcohol, benzene, and chloroform, but insoluble in water and in sulphuric, nitric and hydrochloric acids, with which it does not combine. It forms, however, a solid compound with hydriodic acid.

(2). The following derivatives of the secondary octyl alcohol, $\text{CH}^3\text{CH}^2\text{CHOH}$ from castor oil (vi. 879; vii. 868) have been prepared by Hans Jahn (*Ber.* viii. 803). The *thiocarbimide*, $\text{CS}=\text{N}-\text{C}^8\text{H}^{17}$, formed from the corresponding amine, $\text{H}^2\text{N}\cdot\text{C}^8\text{H}^{17}$, by Hofmann's reaction (p. 606), is a colourless liquid boiling at 234° , and converted by prolonged contact with ammonia into *octyl thiosinamine*, $\text{NH}^2\cdot\text{CS}\cdot\text{NH}\cdot\text{C}^8\text{H}^{17}$, which crystallises in colourless laminae nearly insoluble in water, more soluble in alcohol and in ether, melting at 112.5° . The corresponding *octylamine*, $\text{C}^8\text{H}^{19}\text{N}$, obtained by treating the thiocarbimide with sulphuric acid, forms a platinochloride, $(\text{C}^8\text{H}^{19}\text{N}\cdot\text{HCl})_2\text{PtCl}_4$, which crystallises in laminae having a golden lustre. The *normal thiocyanate*, $\text{CN}\cdot\text{S}\cdot\text{C}^8\text{H}^{17}$, prepared by heating an alcoholic solution of potassium thiocyanate with the secondary octyl iodide in a reflux apparatus, then precipitating with water, washing, drying, and rectifying, is a liquid smelling like conine and boiling at 142° .

(3). A mixture of iso-primary and iso-secondary octyl chlorides (boiling at $179^\circ\text{--}180^\circ$) is produced by passing chlorine into the vapour of boiling di-isobutyl in diffused daylight. On heating this mixture of chlorides with potassium acetate and glacial acetic acid, there is formed—together with an octylene boiling at 122° , and having a density of 0.7526 at 16° —a mixture of acetates (b. p. $193^\circ\text{--}205^\circ$),

from which by saponification with potash there is obtained a mixture of primary and secondary octyl alcohols distilling between 175° and 187° , and yielding by oxidation the iso-octoic acid above mentioned (p. 1424), together with a ketone. The formulæ of the two alcohols are:



(W. C. Williams, *loc. cit.*)

The *iso-primary alcohol* has a pleasant orange-like odour, and a hot burning taste, remains liquid at -17° , and boils at 179° – 180° under 765 mm. pressure (not reduced). It dissolves in alcohol, ether, and chloroform, sparingly in water, and is separated by water from the alcoholic solution. Its specific gravity compared with that of water at 4° was determined at the following temperatures:—

0°	$\cdot \cdot \cdot \cdot$	0.841	40°	$\cdot \cdot \cdot \cdot$	0.814
12°	$\cdot \cdot \cdot \cdot$	0.833	50°	$\cdot \cdot \cdot \cdot$	0.807
20°	$\cdot \cdot \cdot \cdot$	0.828	100°	$\cdot \cdot \cdot \cdot$	0.767
30°	$\cdot \cdot \cdot \cdot$	0.821			

Its vapour-density ($H=1$) was found by experiment to be 66.02; by calculation 65.0.

The *iso-secondary alcohol* is obtained in much smaller quantity, and is much more difficult to separate from traces of undecomposed chloride. It boils at 160° – 163° under 755 mm. pressure, and remains liquid at -17° . It differs from the *iso-primary alcohol* by having a fainter smell, a lower specific gravity, and a larger coefficient of expansion.

Temperature	$\cdot \cdot \cdot \cdot$	15°	30°	40°	50°
Sp. gr.	$\cdot \cdot \cdot \cdot$	0.820	0.811	0.801	0.793
Vapour-density ($H=1$); exp. 65.38; calc. 65.0.					

The ketone, $\text{C}^{11}\text{H}^{18}.\text{CO}.\text{C}^3\text{H}^7$, formed by oxidising the secondary alcohol with a cold mixture of potassium dichromate and sulphuric acid, has a density of 0.865 at 14° , and boils under 743.1 mm. pressure at 159° – 161° . It remains liquid at -17° , and does not form a crystalline compound with acid sodium sulphite. The chief product of its oxidation is acetic acid, but a small quantity of a higher acid, probably isobutyric acid, is formed at the same time (Williams).

(4). Another *iso-secondary octyl alcohol*, probably having the constitution $(\text{C}^3\text{H}^7)_2\text{CH}.\text{CHOH}.\text{C}^3\text{H}^7$, is formed by treating bromoacetyl bromide with zinc-ethyl and decomposing the product with water. It is slightly soluble in water, remains liquid at -30° , and boils at 164° – 168° (Winogradow, *Liebigs Annalen*, xcvi. 125).

OCTYLENES, C^8H^{16} . An octylene is obtained, together with iso-octyl acetate, when the mixture of chlorides resulting from the chlorination of octane (p. 1425) is heated to 200° in sealed tubes with potassium acetate and glacial acetic acid. On extracting the contents of the tubes with water, drying the resulting liquid over potassium carbonate, and subjecting it to fractional distillation, one-third passed over below 130° , the remainder, consisting of iso-octyl acetate, at 193° – 205° . The lower fraction, treated with potash to remove traces of the acetate, yields octylene, having a density of 0.7526 at 16° , and boiling at 122° (Williams).

An octylene is also obtained, together with other hydrocarbons, by the action of dilute hydrochloric acid on spiegeleisen (p. 1064).

CENANTHOL, $\text{C}^6\text{H}^{13}.\text{CHO}$. See HEPTOIC ALDEHYDE (p. 1022).

CENANTHYLIC or NORMAL HEPTOIC ACID, $\text{C}^7\text{H}^{14}\text{O}^2 = \text{CH}^3(\text{CH}^2)^5.\text{COOH}$. Several derivatives of this acid have already been described under HEPTOIC ACIDS (pp. 1021, 1023). The following have been obtained by A. Helms (*Ber.* viii. 1167).

Monobromocenanthylic acid is formed by heating 1 mol. bromine and 1 mol. cenanthylic acid together at 140° – 160° , but has not been isolated in the pure state.

Amidoceananthylic acid, $\text{C}^7\text{H}^{13}(\text{NH}^2)\text{O}^2$, formed by saturating an alcoholic solution of bromocenanthylic acid with ammonia, and digesting it for three or four hours in the water-bath, separates on cooling in crystals, which may be purified by washing with alcohol, conversion into lead salt, separation therefrom by hydrogen sulphide, and recrystallisation from weak spirit. It is thus obtained in hexagonal tables or laminae, soluble in water and weak spirit, but not in absolute alcohol or ether. When heated, a small portion only volatilises without decomposition, the greater part being carbonised, with evolution of alkaline vapours. The *copper salt* is a dark blue amorphous powder, nearly insoluble in water, alcohol, and ammonia. A

Table for the Detection of the Fat Oils.

	At the ordinary temperature.			After boiling.			
	Snow-white : Almond oil : good rape oil, bleached. Olive oil.	Yellowish : Poppy oil, olive oil, Sesame oil.	Greenish : Lined oil : hemp oil; oils containing copper, and arti- ficially coloured oils.	Rose : Refined rape oil.	Brown and solid : Hemp oil.	Yellowish-brown fluid : Lined oil.	Red : Train oil.
Equal volume of oil and fuming red nitric acid are carefully poured into a test-glass. At the point of contact a ring is formed, and this is—	Small and bright green, the oil itself is floccy and non- transparent. Almond oil.	Dark green, rose- coloured above. Poppy oil.	Broad and beautifully bright bluish- green. Olive oil.	Brown-red : Cod-liver oil.	Green, red above. Lined oil.	Brownish - red, greenish be- low. Rape oil.	The whole of the oil is after a time coloured red. Lined oil.
	10 drops of oil and 2 drops of acid.			Equal volumes of oil and acid.			
				Without carbon sulphide.			
				With carbon sulphide.			
The oil is mixed with pure concentrated sulphuric acid in a test-glass; the point of contact between the two is coloured :	Fine green, with brown streaks. Rape oil.	Yellow, on shaking, brownish olive- green. Poppy oil.	Red, soon passing into serpentine black streaks. Train oil.	After shaking, fine full dark green. Rape oil.	Green : Lined oil. Hemp oil.	Red : Train oil.	With twenty times its volume of carbon sulphide, beautiful violet, quickly turning brown. Train oil.
By the elaidine test the oil becomes :—	Solid, curly white olive oil : almond oil : bleached rape oil	Solid, curly, yellow. Rape oil.	Solid and red. Sesame oil.	Wax-like white. Castor oil.	Streaks and drops of oil show them- selves in the elaidine; a mix- ture containing drying oils.	Unchanged : Lined oil, Poppy oil, Nut oil.	Ethereal oils added to improve smell of olive oil swim on top of the elaidine.
By boiling with lead oxide and water, a plaster is formed, the consistency of which is :—	Solid. Olive oil.	Greasy : rape almond oil : Sesame oil.	Greasy, but drying after a time. Drying oils.	—	—	—	—
Solubility of one part of oil in alcohol :—	1 : 1 Castor oil.	1 : 25. Poppy oil.	1 : 30. Hemp oil.	1 : 40. Lined oil.	1 : 60. Almond oil.	—	—
Specific gravity :	913. Poppy oil, and oil of <i>Brassica napus</i> .	914. Almond oil, and oil of <i>Brass. Camp.</i>	928. Olive oil.	923. Sesame oil.	926. Sunflower oil.	930-970. Castor oil.	930. Lined oil.
Temperature of liquefaction Centigrade :	—27°. Hemp oil.	—18°. Castor oil. +25°. Olive oil.	—18° to —20°. Lined oil. —20° to —25°. Almond oil.	—16°. Sunflower oil.	Oil of <i>Brassica napus</i> .	—4°. Oil of <i>Brassica campestris</i> .	—5°. Sesame oil.

solution either by titration with potash, &c., or by measuring with a hydrometer the increase of sp. gr. of the alcohol arising from the presence of the acid.

Estimation of Mineral Oil or Paraffin Wax in other Fats or Oils.—For this purpose the oil is saponified with an alcoholic solution of caustic soda, and the unsaponified oil or wax is separated with petroleum spirit. 200 pts. of the oil are placed in a basin with 350 pts. of an alcoholic caustic soda-solution (strength, 9 per cent. Na_2O), and boiled until the mixture begins to froth. 200 pts. of methylated spirit are added to dissolve the soap, &c., 90 pts. of sodium bicarbonate to convert any caustic soda into carbonate, and finally 500 pts. of washed and ignited mortar sand. The mixture is boiled for a few minutes, and then the alcohol and water are distilled off from a water bath. The residue when cold is transferred to a wide-mouthed stoppered bottle, and shaken with petroleum spirit; the sand and soap are allowed to settle; the spirit containing the wax and mineral oil is drawn off and filtered through asbestos; the residual soap and sand is thrown on a cloth; and the liquid pressed out. The petroleum spirit is distilled from the mineral oil at 100° , and the residue transferred to a flask, with a hole blown in the side, which is fitted with a cork bearing a thermometer and small piece of glass tubing; the whole is previously weighed; and the last traces of spirit are distilled at 220° ; dry air is then blown through; and the whole is weighed. Certain corrections have to be made, in consequence of oil capable of saponification containing small quantities of non-saponifiable oil soluble in petroleum spirit. The correction in the case of Russian tallow amounts to '64 per cent. (W. Thomson *Chem. News*, xxviii. 167).

Solubility of Fixed Oils in Glacial Acetic Acid.—The following determinations have been made by J. B. Barnes (*Pharm. J. Trans.* [3], vi. 221):

1 vol. Glacial Acetic Acid dissolves	7 vols. Fixed Oil of Almonds
1 " " "	8 " Olive Oil
1 " " "	7 " Cod-liver Oil
1 " " "	7 " Linseed Oil
2 " " "	1 " Turpentine Oil
20 " " "	1 " Copaiba Oil
1 " " "	2 " Lemon Oil
1 " " "	1 " Juniper Oil

Castor oil and croton oil are dissolved by glacial acetic acid in all proportions.

Action of Fixed Oils on Copper.—W. H. Watson (*Chem. News*, xxxvi. 200), by exposing 8 square inches of copper surface to 500 grain-measures of various oils, has obtained the following results:—

	Grains of Copper in Solution	
	after 10 days	after 77 days
Linseed	0.3	0.5435
Olive	0.22	0.24
Colza	0.017	0.14
Almond	0.103	0.22
Seal	0.0485	0.08
Sperm	0.003	0.06
Castor	0.0065	0.01
English Neat's-foot	0.11	—
Sesame	0.17	—
Paraffin	0.0015	0.003

See also COPPER (p. 558).

Lubricating Oils.—The mineral lubricating oils known as 'Vulcan oil' (petroleum of sp. gr. 0.87–0.89 purified by sulphuric acid and mixed with 5 per cent. rape-oil), and 'Opal-oil' (petroleum of sp. gr. 0.85–0.87, purified in like manner and mixed with rape-oil), have not been found to act well as lubricators for parts of machinery which move with great rapidity, such as railway axles, spindles, &c. Better results are obtained with purified 'rosin-oil.' The strong odour of this oil and its liability to deposit rosin are removed as follows: 100 pounds of dry thick rosin-oil are heated in a pan till of thin fluidity. The fire is then removed, and 3 pounds of fuming sulphuric acid are gradually dropped in, with constant stirring. After half an hour's mixing, the oil is left to stand for twelve hours, then drawn off by a siphon into a wooden vat, washed with hot water, and drawn off after twelve hours' settling, the washing being repeated till the water runs off without acid reaction. After several days' separation, a dark yellow, faintly odorous rosin-oil is obtained without blue reflex. This oil, mixed with olive or rape oil, may be used advantageously for lubricating the heavy parts of machinery.

To obtain the oil perfectly free from odour, and of clear yellow tint, the dark

yellow rosin oil is run into a flask or globe; 1 pound of water is added to 100 pounds of it; the whole is well shaken; and 8 pounds of hydrochloric acid diluted with 10 pounds of water are gradually stirred in. To this mixture 1 pound of red lead and 5 pounds of dilute hydrochloric acid are added; the whole is frequently shaken; and after some days the oil is drawn off, washed with water till free from acid, and set in the sunlight for about eight days in the flask. Thus treated it becomes of a light yellow tint.

The yellow rosin oil, when mixed with one-third of rape or olive oil, yields a good lubricating oil for all machine purposes, as it does not deposit rosin; it can also be mixed with petroleum (B. Hoffmann, *Dingl. pol. J.* c. viii. 237).

OILS, VOLATILE. *Estimation.*—The following method is given by O. Osse (*Arch. Pharm.* [3], vii. 104). The oil is dissolved in petroleum spirit distilling below 40° , and evaporated in a watch-glass in a current of carefully dried air until nearly every trace of petroleum spirit is removed. It is then left to evaporate spontaneously in the open air, and weighed at the end of every minute. When the loss in weight during one minute becomes constant, this loss is considered to represent the evaporation-constant from which to correct the weight of oil obtained. This correction is effected by adding to the weight of the oil when the loss in weight became constant, the amount of the constant loss multiplied by the number of minutes during which the oil has been previously allowed to evaporate in the open air.

The method has been applied to the determination of the percentage of volatile oils in the aromatic waters of pharmacy, and of the solubility of these oils in water.

In presence of resinous or fatty substances, after the total amount of the mixed volatile oil and resinous or fatty bodies has been determined as above, the weight of these last can be found by heating the whole to 110° for an hour or two to drive off all the volatile oil. By these means the following determinations were made:

	Volatile oil	Fatty and resinous bodies
	1.75 per cent.	2.25 per cent.
Buchu leaves. . . .	13.25 "	25.00 "
Laurel	2.50 "	4.50 "
Cascarilla	13.00 "	13.50 "
Indian Anise	24.75 "	1.75 "
Clove		

On the Adulterations of Volatile Oils, see Leonhardi (*Arch. Pharm.* [3], xii. 490; *Chem. Soc. J.* xxxiv. 811).

Oxidation.—Volatile oils and other volatile organic bodies are rapidly oxidised by a mixture of potassium permanganate and strong sulphuric acid, in some cases with inflammation and explosion. The best way of producing the effect is to place 10 or 12 drops of the oil on a capsule; and touch it with a glass rod, the end of which has been dipped into the oxidising mixture just mentioned. The following oils then burn with explosion: *Thyme, mace, rectified turpentine, valerian, cassia, wild marjoram, rue, cubebs, lemon.* The following mostly take fire without explosion, especially if a small quantity be dropped on bibulous paper and then touched with the mixture: *Oil of rosemary, lavender, cloves, rose, geranium, gaultheria, caraway, cajeput, bitter almonds, and rectified coal-oil.*

The oxidising properties of *turpentine oil* and other volatile oils which have been exposed to the air—formerly attributed to the presence of ozone—was shown by Kingzett in 1874 to be due to the formation of an oxidised organic compound which readily gives up a portion of its oxygen. This compound from turpentine oil was at first supposed to be monohydrated terpene oxide (vii. 887); but from later experiments (*Chem. Soc. J.* xxviii. 210; xxxiv. 127, 135), Kingzett infers that it is the peroxide of the radicle of camphoric acid, $C^{10}H^{14}O^2$, which, however, has not yet been isolated. The aqueous solution obtained by shaking up the oxidised oil with water, or dissolving it in alcohol and precipitating with water, contains hydrogen dioxide, resulting from the decomposition of the originally formed organic peroxide, together with formic, acetic, and camphoric acids. This solution exhibits powerful antiseptic properties due to the hydrogen dioxide and camphoric acid. Evaporated to dryness over the water-bath, it leaves a dark-coloured substance having, when hot, a sugar-like odour and viscid consistence, and solidifying on cooling to a firm but adhesive mass, which, when treated with strong sulphuric acid, gives a colour somewhat resembling that obtained in Pettenkofer's bile reaction. This substance, whose composition may be represented by the empirical formula $C^{10}H^{14}O^2$, is for the most part soluble in hot water, about 5 per cent. remaining as a viscid, insoluble, nearly black substance having the same composition (Kingzett, *Chem. News*, xxxix. 279).

OKENITE. The relations between okenite (iv. 191), centrallassite (i. 822), and

gyrolite (ii. 963) have been examined by H. How (*Phil. Mag.* [5], i. 128), who represents these minerals by the following formulæ :

Okenite	$\text{CaSi}^2\text{O}^6.2\text{H}^2\text{O} = \text{CaO}.2\text{SiO}^2.2\text{H}^2\text{O}$
Centrallussite	$\text{Ca}^2\text{Si}^2\text{O}^6.2\text{H}^2\text{O} = 2\text{CaO}.3\text{SiO}^2.2\text{H}^2\text{O}$
Gyrolite	$\text{Ca}^2\text{Si}^3\text{O}^6.3\text{H}^2\text{O} = 2\text{CaO}.3\text{SiO}^2.3\text{H}^2\text{O}$

OLEFINES, C^nH^{2n} . *Synthesis.*—By heating a mixture of amylene and methyl iodide with excess of dry lead oxide at 210° for several hours, a product boiling between 36° and 85° is obtained, one-third of which comes over between 70° and 83° , and consists of a mixture of C^6H^{12} and C^7H^{14} ; this portion forms with bromine a solid compound, apparently $\text{C}^6\text{H}^{12}\text{Br}^2$, melting at 139° – 140° . The hydrocarbons dissolve in sulphuric acid (2 acid to 1 water), and on the addition of water a liquid and a solid body separate out. The latter, which is the hydrate, $2\text{C}^7\text{H}^{14}\text{O} + \text{H}^2\text{O}$, of Butlerow's *pentamethylethol*, melts at 75° . The action of fuming hydrochloric acid on the mixed olefines also gives rise to a solid product, melting at 100° and boiling at 120° – 125° , which appears to be a mixture of $\text{C}^6\text{H}^{12}\text{Cl}$ and $\text{C}^7\text{H}^{14}\text{Cl}$.

Olefines are also formed by the action of lead oxide on alcoholic chlorides, bromides, and iodides, at 220° . Isobutyl iodide is thus completely decomposed: $2\text{C}^4\text{H}^9\text{I} + \text{PbO} = 2\text{C}^4\text{H}^8 + \text{PbI}^2 + \text{H}^2\text{O}$, and isopentyl iodide gives a pentylene isomeric with that obtained by the action of alcoholic potash (Éltékoff, *Ber.* xi. 112).

Action of Hydrochloric Acid.—From the action of hydrochloric acid on the butylenes, pentylenes, and hexylenes, Le Bel (*Compt. rend.* lxxxv. 832) infers that the olefins of the constitution $\text{CH}^2=\text{CRR}'$ and $\text{CHR}=\text{CRR}''$, in which R , R' , and R'' , are different or the same alcohol-radicles, combine with hydrochloric acid in the cold, whereas those of the constitution $\text{CH}^2=\text{CHR}$, and probably $\text{CHR}=\text{CHR}'$, are not attacked thereby. This conclusion, however, requires to be verified by further examples.

Action of Sulphuric Acid. Polymerisation.—From experiments by Gorianow a. Butlerow (*Liebig's Annalen*, clxix. 146), it appears that ethylene is not absorbed by strong sulphuric acid at ordinary temperatures, but that at 100° , or better at 160° – 175° , rapid and complete absorption takes place; and on subsequently distilling the liquid with a sufficient quantity of water, and treating the distillate with potassium carbonate, ethyl alcohol is obtained. In Berthelot's well-known experiment, the violent and continued shaking doubtless served, not only to bring the gas into intimate contact with the liquid, but likewise to develop the heat required to induce the absorption.

Contact of ethylene with sulphuric acid, at the temperatures above mentioned, did not result in condensation of the hydrocarbon. Neither did a still further elevation of temperature or the employment of fuming sulphuric acid or of fluoride of boron produce signs of polymerisation. This remarkable stability in circumstances under which its higher homologues are easily affected, indicates that the constitution of ethylene is symmetrical, and not analogous to that of propylene, isobutylene, &c.

Propylene and isobutylene are readily polymerised by the action either of sulphuric acid or of boron fluoride. A preliminary experiment with isobutylene gave, besides trimethyl-carbinol, oily condensation products, a fraction of which boiled at 173° – 176° , and had a vapour-density corresponding with the formula $\text{C}^{12}\text{H}^{24}$. *Di-isobutylene* did not appear to be formed under these circumstances.

Action of Oxidising Agents.—O. and F. Zeidler (*Liebig's Annalen*, cxvii. 143) have examined the reactions exerted on the olefines by the following oxidising agents: (a) an aqueous solution of potassium permanganate; (b) a solution of potassium permanganate acidified with sulphuric acid; (c) an alkaline solution of potassium permanganate; (d) a solution of chromic acid; and (e) a mixture of potassium dichromate and sulphuric acid. In each case 2–3 litres of the gaseous olefine were used, and the proportion of oxidising agent is taken so as to represent 4 mols. of oxygen to 1 mol. of olefine.

Ethylene yielded the following results:—With (a) formic, acetic, and oxalic acids; (b) carbonic, formic, acetic, and oxalic acids (traces); (c) carbonic, formic, acetic, and oxalic acids; (d) no action at the ordinary temperature but at 100° carbonic acid, and small quantities of formic, acetic, and oxalic acids are formed; (e) the same as (d). These results differ somewhat from those obtained by Truchot (*Annalen*, cxli. 108); Berthelot (*Compt. rend.* lxi. 35; *Annalen Suppl.* v. 95; *Compt. rend.* lxxviii. 333; *Annalen*, cl. 373; *Ann. Chim. Phys.* 1875 [5], vi. 449); and by Chapman a. Thorpe (*Annalen*, cxlii. 182).

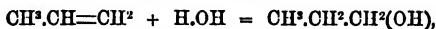
Propylene yielded (a) carbonic, oxalic, and acetic acids, and traces of an acid, perhaps succinic or malonic acid; (b) carbonic, acetic, oxalic acids, a little formic acid, and traces of an acid which may be either malonic or glycollic acid; traces of acetone;

(c) carbonic, acetic, oxalic acids, traces of formic acid, and probably malonic acid, also a small quantity of acetone; (d) small quantities of carbonic acid, but large quantities of formic and acetic acids, and only a trace of oxalic acid; (e) the same result as (d).

Isobutylene, $\text{CH}^3\text{C}=\text{CH}^2$, prepared from fermentation butyl iodide, yielded the following results:—(a) carbonic acid, small quantities of acetic and formic acids, and, as chief product, oxalic acid; (b) carbonic, formic, acetic, and oxalic acids; (c) carbonic, small quantity of formic, acetic, and oxalic acids; (d) no action in the cold, only at the temperature of steam-bath, yielding carbonic, formic, acetic, and oxalic acids, also acetone; (e) the same as (d), the action is, however, more energetic. *Isobutylene* does not in any case yield succinic acid.

F. Zeidler (*Annalen*, clxxvi. 247) obtained by the oxidation of amylene, b. p. 35° , butyric and succinic acids. Since then, Wischnegradsky (*Annalen*, cxc. 328) has shown that this olefine consists of two isomerides, one of which is trimethylethylene, and the other either propylethylene or ethylmethylethylene. The latter (b. p. 35° – 37°), prepared from ordinary amylene by means of its insolubility in sulphuric acid, yields on oxidation with an alkaline solution of potassium permanganate, succinic and oxalic acids, also formic and butyric acids, and traces of carbonic acid. These results show the constitution of this amylene to be $\text{CH}^3\text{CH}^2\text{CH}^2\text{CH}=\text{CH}^2$, i.e. propylethylene, and not ethylmethylethylene (see AMYLENES, p. 81).

The difference in action of the several oxidising agents on the olefines is a difference, not of kind, but only of degree; in other words, it is quantitative, but not qualitative. Moreover, the olefines are attacked at the point of double union, and the resulting monobasic acids are, as shown by P. de St. Gilles (*Compt. rend.* xlv. 811) and Berthelot (*Annalen*, Suppl. v. 95; vi. 181), further oxidised to dibasic acids. The formation of acetic acid from ethylene, and of malonic acid from propylene, may be explained by supposing the addition of water as H and OH to take place; for instance, in the case of ethylene, a primary alcohol would be first formed, and the molecule not broken up. In the case of propylene, the addition may take place so as to form the primary or secondary alcohol, which by further oxidation may yield malonic acid and acetone.



or



Formation of Glycols, Aldehydes, and Ketones from the Haloid Compounds of the Olefines.—The haloid compounds of ethylene, when heated with water and lead oxide, yield glycol and aldehyde, whilst propylene chloride and bromide, under the same circumstances, yield propyl-glycol, acetone, and propaldehyde. Similarly isobutylene bromide yields isobutyl-glycol and the corresponding aldehyde, and trimethylethylene bromide yields isopropylmethyl ketone. These results show that the first product of the action in every case is a glycol, which by elimination of water is partially or entirely converted into aldehyde or ketone (Eltekoff, *Ber.* xi. 989).

Decomposition of Olefine Bromides, $\text{R}'\text{Br}^2$, by the Copper-zinc couple and by Zinc alone.—The decomposition of ethylene bromide by zinc and by the couple has been already described (vii. 489). *Propylene* and *amylene bromide* are decomposed in the same manner, the action in all cases being a simple abstraction of the bromine by the zinc and liberation of the olefine. In the case of propylene bromide the dry couple produces very little decomposition, but the action is facilitated by water, as with ethylene bromide. Zinc alone acts but slightly when wetted with water, but in presence of alcohol it decomposes the bromide rapidly after about 17 minutes' contact. *Amylene bromide* is not attacked by the couple wet with water at 15° , but rapid action takes place at 60° . In contact with alcohol, zinc alone effects the same decomposition at ordinary temperatures (Gladstone & Tribe, *Chem. Soc. J.* xxvii. 408).

OLEIC ACID, $\text{C}^{18}\text{H}^{34}\text{O}_2$. When a mixture of glacial acetic acid and water is gradually added to an alcoholic solution of *oleic acid*, a point is reached at which the oleic acid remains entirely dissolved, but is completely separated by the addition of one-tenth of a c.c. more of the acid, whereas *stearic acid* in alcoholic solution begins to precipitate as soon as the acetic acid is added, and is entirely insoluble in a mixture of alcohol and acetic acid, and even in presence of oleic acid. This difference of behaviour affords the means of separating and estimating the two acids in mixtures produced by the saponification of fats (J. David, *Compt. rend.* lxxxvii. 1416; *Chem. Soc. J.* xxxiv. 1011).

Conversion into Stearic Acid.—This conversion may be effected by heating oleic acid with hydriodic acid (b. p. 127°) and amorphous phosphorus to 200° – 210° in a sealed tube for eight hours, then opening the tube to allow hydrogen phosphide to escape, resealing it, and heating it again. By this treatment the liquid oleic acid is

completely converted into a crystalline mass of stearic acid, which may be purified by melting it under water, recrystallising it from hot alcohol, treating it with sodium-amalgam to remove any small quantity of iodine that it may retain, and once more crystallising it from alcohol (G. Goldschmiedt, *Wien. Akad. Ber.* lxxii. 366). See also M. A. Muter (*Analyst*, ii. 73).

Mercury Oleate.—For the preparation of this salt from mercuric oxide and oleic acid, A. Hilger (*Arch. Pharm.* [3], iii. 490) recommends the use of mercuric oxide prepared in the wet way and dried as quickly as possible. The temperature of the mixture should not be allowed to rise above 70° , otherwise reduction of the mercuric oxide will take place. The preparation containing not more than 15 to 16 per cent. mercuric oxide forms viscid masses of yellow to red-brown colour. As the proportion of mercuric oxide increases, the mixture acquires an unctuous consistence, and when more than 30 per cent. HgO is added, immediate decomposition takes place, attended with separation of mercury. The same decomposition appears to take place after long keeping in preparations containing smaller proportions of the oxide. It does not appear possible to prepare pure mercury oleate by double decomposition. See also C. Rice (*Pharm. J. Trans.* [3], iii. 582; vi. 147; *Chem. Soc. J.* xxvi. 510).

OLENES. Syn. with OLEFINES.

OLIBENE, $\text{C}^{10}\text{H}^{14}$. A volatile oil obtained from incense. This substance, distilled with water, yields an oil which passes over at 160° – 170° ; and this oil is resolved by fractional distillation into olibene boiling below 160° , and a small portion of an oxygenated oil which boils above 175° . Olibene, treated with dry hydrochloric acid gas, forms a crystalline hydrochloride, smelling like camphor, easily soluble in alcohol, melting at 127° . The resin of incense appears therefore to consist of condensation-products of a terpene (Kurbatow, *Liebig's Annalen*, clxxiii. 1).

OLIGOCLASE. The following analyses of this mineral have lately been published in addition to those given under FELSAPAR (pp. 773, 774): 1. From Unionville, Pennsylvania, occurring in yellowish and brown-white grains, in a few instances with recognisable and then striated cleavage-faces; enclosing corundum and a second mineral, probably spinel; analysed by Chatard (*Jahresb. f. Chem.* 1873, 1152). 2. From the granitic gneiss of New York. Sp. gr. 2.644 (P. Schweitzer, *Am. Chemist*, iv. 444). 3. From the lava of Santorin, which is rich in oligoclase. Sp. gr. 2.620 (Fouqué, *Compt. rend.* lxxx. 631). 4. From the graphite-garnet gneiss, called *Kinzigit*, of Schenkzenzell near Wittichen in the Schwarzwald (Hebenstreit, *ibid.* 417).

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	
1.	59.35	24.16	0.61	—	3.08	0.34	3.78	7.22	1.96	= 100.50
2.	63.36	22.28	—	0.67	4.24	—	0.96	8.14	0.40	= 100.05
3.	59.7	23.2	0.4	—	7.9	1.0	0.8	6.6	—	= 99.6
4.	62.90	22.23	trace	—	4.45	—	2.09	8.48	—	= 100.15

On the action of water containing carbonic acid on Oligoclase, see MINERALS (p. 1329).

OLIVE OIL. *Extraction.*—The calcareous soil of the district of Sahil in Tunis is very well adapted to the culture of the olive. In this district there are five million olive-trees, which, if the winter and spring rains occur in normal amount, yield annually 40,000 tons of oil. The gathering of the olives takes place in December and January. The olives are crushed between horizontal millstones; the pulp is immediately thrown into water; and the oil which then comes to the surface is sold as best quality (*Drab-el-ma*). By pressure a strong-smelling oil of inferior quality (*Masri*) is obtained. The press-cakes are used as fodder for camels. The quantity of oil exported from Tunis in five years (1869–73) represented a value of 300,000*l.* sterling.

Testing.—The following method of testing the purity of olive oil by means of its conversion into solid elaidin was given by E. Kopp (*Deut. Chem. Ges. Ber.* viii. 979). 10 vols. of the oil and 1 vol. ordinary nitric acid are introduced into a test-tube together with a few pieces of copper wire; and as soon as the gas-bubbles begin to pass somewhat rapidly through the supernatant oil, the acid and oil are intimately mixed by stirring with a glass rod, the mixture then left to itself for a few minutes, and the separated liquids again mixed by stirring and heating. If it be then left in a cool place, the oil after some time begins to solidify, the solidification being quicker in proportion as the oil is purer. In mixtures with other oils the solidification is much slower, and the elaidin formed, instead of being white and hard, is soft, and has a more or less yellowish or brownish colour.

On the Detection of Earthnut Oil in Olive Oil, see vol. vii. p. 443.

On the Characters by which Olive Oil is distinguished from other Fixed Oils, see Glössner's table (p. 1428).

OLIVES. The following analyses of the fruit and leaves of the olive, 'Blanquet' variety, collected at intervals of a month from May 30 to November 30, are given by A. Roussille (*Compt. rend.* lxxxvi. 610).

Composition of the leaves	May 30	June 30	July 30	Aug. 30	Sept. 30	Oct. 30	Nov. 30
Fat and chlorophyll . . .	5·432	4·330	4·578	4·577	3·631	3·766	3·702
Nitrogenous substance . . .	8·755	8·162	9·337	8·275	7·883	8·287	8·443
Lignin	18·886	16·444	18·833	20·778	27·709	27·514	28·117
Ash	7·777	7·217	6·987	8·091	6·610	6·848	5·861
Unestimated	59·130	63·847	60·265	58·279	54·207	53·585	53·877
Alkaline salts	10·794	19·795	22·190	8·992	12·849	16·834	19·006
Earthy phosphates	12·938	27·005	22·360	8·604	9·754	11·127	12·304
" carbonates, &c.	70·554	49·820	46·410	75·606	72·483	69·009	65·740
Silica	5·714	3·380	9·040	6·798	4·918	3·030	2·950

Composition of the pulp of the fruit	June 30	July 30	Aug. 30	Sept. 30	Oct. 30	Nov. 30
Water	22·003	60·690	66·051	56·005	51·688	50·198
Fat and chlorophyll	1·397	5·490	29·190	62·304	67·213	68·573
Nitrogenous substance	—	—	14·619	4·189	4·411	4·329
Lignin	—	—	13·341	7·432	7·072	6·096
Ash	—	—	4·156	2·736	2·964	3·060
Unestimated	98·603	94·510	38·694	23·339	18·340	17·940
Alkaline salts	—	—	81·818	82·500	86·353	85·916
Earthy phosphates, &c.	—	—	16·642	16·250	13·068	13·615
Silica	—	—	1·540	1·250	0·579	0·469
P ² O ⁵ in the alkaline salts	—	—	1·675	4·421	4·784	5·164

Fatty Matter and Chlorophyll.—The chlorophyll, which is very abundant in the leaves at the end of May, gradually diminishes in quantity; it does not migrate to the fruit.

Nitrogenous Matter.—In the leaves, the nitrogen increases until the end of July. In August it greatly diminishes, and accumulates in the pericarp. A migration of nitrogen in the fruit then takes place, probably going to the endosperm, for the amount diminishes two-thirds by the end of September. Afterwards (when the kernel should be forming) the proportion slightly increases in both leaves and fruit.

Lignin.—In the leaves, this substance decreases in June, after which it continues to increase.

Mineral Matter.—In the leaves, the mineral matter increases to the end of August, and then diminishes until the fruit ripens. The proportion of alkaline salts increases until the end of July: in August it goes to the fruit, forming the chief mineral constituent. A steady increase in the leaves again takes place, and continues until the fruit is gathered. Magnesium and calcium phosphates increase in the leaves until July, rapidly diminishing in August, as is the case with the alkaline salts. It appears that the migration of the phosphates precedes that of the alkalis, corresponding with the migration of the nitrogenous matter; whereas that of the alkaline salts corresponds with the non-azotised proximate principles, and to their conversion into fatty substance. In the fruit, the mineral matter reaches its maximum by the end of August, and then diminishes, but again gradually increases as it ripens. The alkaline salts increase with the fatty matter in almost a definite proportion with the potassium phosphate, thus (combined with potassium):—

1·675 P ² O ⁵ at the end of August	with 29·190 fat.
4·421 " " " September	" 62·304 "
4·784 " " " October	" 67·213 "
5·164 " when the fruit was gathered	" 68·575 "

The calcium and magnesium phosphates are at their maximum in August, at the same time as the nitrogenous matter. Phosphoric acid can enter the endosperm only in the form of alkaline phosphate.

Silica.—Probably an accidental impurity.

OLIVIL. When pure olivil (m. p. 119° – 120°), obtained from the gum of the olive-tree (iv. 200), is digested for an hour with concentrated hydriodic acid (b. p. 127°), a mixture of the iodides of methyl and ethyl is obtained, together with a black non-volatile solid substance of glistening aspect. This substance is insoluble in water, only slightly soluble in ether, but readily soluble in alcohol, especially when hot, and precipitated therefrom by water (D. Amato, *Gazz. chim. ital.* 1878, 83).

OLIVINE. The following are recent analyses of this mineral: 1. Transparent pale-yellow olivine, sp. gr. 3.261, from Vesuvius (E. v. Dingelstedt, *Jahrb. f. Min.* 1874, 86). 2. Small, light brownish crystals, sp. gr. = 3.183, occurring, together with humite, in the geodes of a block ejected from Vesuvius (G. vom Rath, *Berl. Akad. Ber.* 1874, 745). 3. From the basalt of Kosakov (Farsky, *Verh. geol. Reichsanst.* 1876, 205). 4. From the basalt of the Lützelberg, a mountain of the Kaiserstuhl range, where it occurs, to the amount of 78 per cent., in nodules together with chrome-iron ore and two pyroxenes, viz. a chrome diopside and a mineral nearly allied to bronzite (A. Knop, *Jahrb. f. Min.* 1877, 697). 5. From the palæopierite of the Black Stones of Nassau (K. Oelbecke, *ibid.* 844).

	SiO ²	MgO	CaO	FeO	NiO, CaO	MnO	CrO	Cr ² O ³	Al ² O ³	
1.	42.30	51.64	1.08	5.01	—	—	—	—	0.42	= 100.45
2.	39.93	48.70	—	8.43	—	1.03	—	—	0.10	= 98.19
3.*	41.22	49.36	—	9.13	0.24	0.16	—	0.05	0.14	= 100.30
4.	41.2	49.7	—	8.7	—	—	—	—	—	= 99.6
5.	42.53	35.68	14.09	6.48	—	—	—	—	—	= 98.78

Relations between Olivine and Serpentine.—Olivine occurring in small granules in the serpentine of Snarum, the well-known locality of pseudomorphs of serpentine after olivine, has been analysed, together with the accompanying serpentine, by A. Helland (*Pogg. Ann.* cxlviii. 329):

	SiO ²	MgO	FeO	CrO	Al ² O ³	Loss by ignition	Sp. gr.
Olivine . . .	41.32	54.69	2.39	0.05	0.28	0.20 =	98.93
Serpentine . .	42.72	42.52	2.25	trace	0.06	13.39 =	100.94

Supposing that the conversion of the olivine into serpentine has taken place without alteration of volume, and taking into account the difference of density of the two minerals, the weights of the two in grams contained in 1 cubic centimeter of substance will be as follows:

Olivine . . .	1.345	0.009	0.078	0.002	1.780	0.006 =	3.220
Serpentine . .	1.071	0.002	0.056	—	1.065	0.336 =	2.530

Increase or Decrease -0.274 -0.007 -0.022 -0.002 -0.715 +0.330

All the other minerals found in the serpentine bed, viz. magnesite, hydrotalcite, quartz, mica, magnetic iron oxide, and titanite iron, may, with the exception of the last, be regarded as secondary products of the transformation process, admitting the access of a small quantity of carbon dioxide (for the magnesite) and of alkalis (for the mica). The titanite iron appears, from the mode of its occurrence, to be a pre-existing mineral.

Several hydrated silicates related to serpentine, and therefore to olivine, have been analysed by F. v. Kobell (*Jahrb. f. Min.* 1874, 733):

1. *Chrysotil* from Zermatt: pale yellow fibrous masses. 2. *Antigorite* from Zermatt: dark grey crystalline monatomic masses. 3. A mineral from Kräbath in Styria, nearly allied to the marmolite of Hoboken: compact, yellowish-white; sp. gr. = 2.13. 4. *Marmolite* from Hoboken: crystallo-laminar.

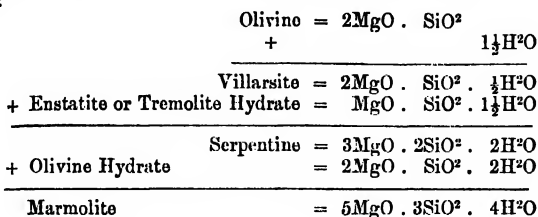
	SiO ²	MgO	FeO	Al ² O ³	H ² O	
1.	42.5	43.0	2.0	—	13.1	= 100.6
2.	42.73	36.51	7.20	1.33	11.66	= 99.43
3.	42.0	38.5	1.0	trace	17.5	= 99.0
4.	42.00	41.00	0.90	0.26	15.00	= 99.16

Also very slight traces of Cr²O³ in 1, of Mn²O³ in 3.

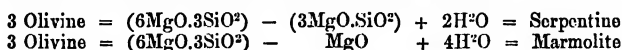
* Mean of three analyses.

According to these results, the minerals in question may be referred to two species, viz. chrysotil and antigorite to *serpentine*, $3\text{MgO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$; vorhausserite (v. 1006) and the Kraubath mineral to *marmolite*, $5\text{MgO} \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$.

The numerical relation of these species to olivine is shown by the following comparison :



The processes of transformation may, however, be equally well regarded as separation, with simultaneous assumption of water, provided that we start, not from one but from several molecules of olivine regarded as pre-existing :



OLIVINE-ROCK. The olivine-rocks of the granulite district of Saxony have been described by H. Möhl (*Jahrb. f. Min.* 1876, 225; *Chem. Soc. J.* xxx. 338); they are of two kinds, *garnet olivine-rock* and *enstatite olivine-rock*, accordingly as garnet or enstatite is the predominating constituent, next to the olivine. Several varieties of olivine-rock, including the *dunite* of New Zealand, the *therzolite* of the Pyrenees, the eruptive rocks of the Fichtelgebirge, of Ellgost in Austrian Silesia, and of the Hessian Hinterland, have been described by H. Möhl (*Jahrb. f. Min.* 1877, 413; *Chem. Soc. J.* xxx. 119).

The following are analyses of olivine-rocks. (1). From the Culsagee Mine near Franklin, Macon County, North Carolina. (2). Rock consisting of serpentinised olivine with plagioclase from the Cullikenee or Buck Creek Mine in Clay County, North Carolina : analysed by Chatard (*Jahresb. f. Chem.* 1873, 1156). (3). Diallogite olivine-rock of Mohsdorf in the Saxon granulite district (Leuchardt, *ibid.* 1876, 1280) (4). Olivine-rock from the Ultenthal (J. R. Müller, *Jahrb. f. Min.* 1877, 739):

	SiO ^a	MgO	CaO	FeO	Fe ² O ³	Al ² O ³	H ² O	
1.	41.58	49.28	0.11	7.49	—	0.14	1.72	= 100.32
2.	35.19	40.99	—	9.70	—	0.64	13.48	= 100
3.	41.99	31.49	1.84	1.66	9.14	6.73	7.09	= 99.94
4.	40.82	45.81	trace	12.35	—	0.86	—	= 99.84

OMPHACITE. Analyses of this mineral have been made by Fikenschor (*Jahresb. f. Chem.* 1874, 1301) and Lüdecke (*ibid.* 1876, 1232): 1. From the eclogite of Obernpferdt, near Schwarzenbach in Saxony. Sp. gr. = 3.263 (Fikenschor). 2. From the glaucophane of the island of Syra (Lüdecke):

	SiO ^a	Al ² O ³	FeO	CaO	MgO	K ² O	Na ² O	H ² O
52.57	9.12	5.32	17.41	12.75	0.28	1.11	0.32	= 99.88
52.63	4.6	11.8	12.8	16.1	—	—	1.69*	= 99.52

* Loss by ignition.

ONYX. Damour (*Compt. rend.* lxxxii. 1086) has analysed a so-called alabaster which, under the name 'Onyx of Tecali,' has lately been largely imported into France from Mexico for the fabrication of ornaments. It is milk-white, yellowish-white, or pale green, sometimes with red-brown veins, and exhibits wavy layers. Sp. gr. = 2.77. A. Direct result of analysis. B. Constituents grouped as carbonates:

	CO ²	CaO	MgO	FeO	MnO	H ² O	
A.	43.62	50.10	1.40	4.10	0.22	0.60	= 99.94
Traces of silica.							
	CaCO ³	MgCO ³	FeCO ³	MnCO ³	H ² O		
B.	89.46	2.92	6.60	0.36	0.60	=	99.94

Damour has found manganese in other limestones, Iceland spar for example.

OPAL. Opal is found, as *perlite* and *fiorite*, in the neighbourhood of San Piero, Elba, in kaolin, also in the form of a crust and globular. At Vallicella, in the same

neighbourhood, opal occurs usually as *hyalite*, in cavities in a granite vein. The opal of Sant' Ilario and San Piero encloses garnets, those of the former locality being light yellow, and those from the latter black (G. Roster, *Jahrb. f. Min.* 1877, 531).

F. M. Endlich describes an opal occurring as a deposit of the Upper Geyser basin on the Firehole River. An analysis by A. C. Peale of a milk-white variety, sp. gr. = 2.4903, gave 95.84 per cent. silica, 2.68 Fe²O³ and 1.50 loss by ignition (= 100.02), with traces of alumina, magnesia, potash, soda, and lithia. A light greenish-brown specimen, of sp. gr. 2.0816, gave 6.3 per cent. water.

An opal containing 8.85 per cent. water, and answering to the formula 3SiO².H²O, when exposed to a stream of dry air at 100°, gave off 5.01 per cent. water very quickly, whereby it was converted into 6SiO².H²O, the rest very slowly. An artificially prepared hydrate, SiO².4H²O, was quickly converted, under similar conditions, into SiO².H²O, less quickly into 6SiO².H²O, the remainder of the water in this case also being given off very slowly.

OPIANIC ACID. } See NARCOTINE-DERIVATIVES (pp. 1383, 1384).
OPINIC ACID. }

OPIMUM. Twelve sorts of opium, analysed by Flückiger (*Pharm. J. Trans.* [3], v. 845), gave the following results:

	I	II	III	IV	V	VI
Ethereal Extract	24.2	21.7	22.0	20.6	14.1	17.4
Crude Narcotine	10.0	9.0	8.5	7.6	7.6	8.0
Wax	14.2	12.7	13.5	13.0	6.5	9.4
Pure Narcotine	4.0	6.1	5.5	4.5	4.7	3.1
Crude Morphine	11.2	11.2	14.2	10.6	14.4	—
Pure Morphine	8.6	4.3	3.5	4.6	6.1	3.8

	VII	VIII	IX	X	XI	XII
Ethereal Extract	20.4	—	25.0	23.7	18.1	23.6
Crude Narcotine	9.7	—	10.2	12.2	9.3	11.6
Wax	10.7	—	14.8	11.5	3.8	12.0
Pure Narcotine	5.4	7.7	6.4	8.7	6.0	8.1
Pure Morphine	3.2	6.07	7.1	5.8	4.3	8.3

I. Patna Opium. II. Indian Opium, 1852–3. III. Akbari Opium. IV. Behar Opium. V. Maliva Opium. VI. Sind Opium. VII. Hyderabad Opium. VIII. Opium from Candeish. IX. Persian. X. Egyptian. XI. Opium from Playford, Suffolk, 1823. XII. English, 1859.

W. D. Howard (*Pharm. J. Trans.* [3], vi. 721) found in a sample of Persian opium said to be perfectly pure:

Morphine	Cocaine	Narcotine	Thebaine	Cryptopine	Papaverine
16.40	0.29	2.50	0.57	0.09	traces per cent.

A cheap sort of Persian opium was found by Proctor (*ibid.* 1024) to contain only 0.25 per cent. morphine. A very hygroscopic variety of Persian opium, examined by Charles (*ibid.* iii. 883) yielded 52 per cent. aqueous extract, and contained 8.4 per cent. morphine, 3.6 narcotine, and a small quantity of glucose.

The ash of Behar opium—a mixture of the ashes of various samples from the Government Factory, Patna.—has been analysed by C. Warden (*Chem. News*, xxxviii. 146). It was of a light grey colour, and contained 0.8575 per cent. of charcoal, which was deducted before calculating the percentage composition, which is as follows:—

Fe ² O ³	CaO	MgO	K ² O	Na ² O	SO ²	P ² O ⁵	SiO ²
1.9839	7.1344	2.3104	37.2405	1.7006	23.1419	10.9021	15.2740

There are also traces of alumina, manganese, carbon dioxide, and chlorine. The sulphuric acid, of which there is an unusually large quantity present, is supposed to be united with the potash and lime.

On the methods of estimating Morphine in Opium, see p. 1338.

On the reaction of Opium-bases with *Iodised Hydriodic Acid*, see ALKALOIDS (p. 55); with *Hydrogen Sulphide*, *Auric Bromide*, *Sodio-aurous Thiosulphate*, *Lead Tetrachloride*, and *Ammonium Molybdate*, see p. 56; with *Sulphuric Acid* and *Ferric Chloride*, see PLANT-BASES.

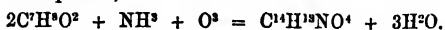
OPOPONAX. See RESINS.

ORANGE-PEEL OIL. See vii. 877.

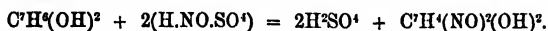
ORCINOL, C⁷H⁸O² = C⁶H⁷(CH³)(OH)². *Orcin. Estimation in Dye-lichens.*—The quantity of orcinol in a dye-lichen may be estimated by titration with bromine-water,

the reagent being added till the suspended precipitate, which for a while has become white, again acquires a yellowish tint, and an excess of bromine is indicated by the smell. The reaction, which is quite definite, consists in the formation of tribromorcinol, so that from the quantity of bromine used (the excess being determined by means of potassium iodide and sodium thiosulphate), it is easy to calculate the quantity of orcinol in the liquid (S. Reymann, *Ber.* viii. 790).

Action of Ammonia.—Liebmann and Troschke (*ibid.* vii. 247), by acting on orcinol with ammonia in contact with the air, have obtained two colouring matters which appear to have the formulæ $C^{14}H^{13}NO^4$ and $C^{14}H^{12}N^2O^3$. The first is probably formed as represented by the equation,



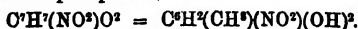
Dinitroso-orcinol, $C^8H^4(NO)^2(OH)^2$ (Stenhouse and Groves, *Chem. Soc. J.* xxxi. 544). This compound is formed, but in small quantity only, by treating orcinol with potassium nitrite and acetic acid; much more readily by the action of nitrosyl sulphate on orcinol:



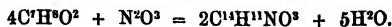
It is advisable to use a solution of nitrosyl sulphate containing 15 per cent. N^2O^3 , prepared in the manner already described (p. 1419), so as to ensure the absence of nitric acid. Of this solution, 100 pts. are added gradually and with continued agitation to 20 pts. of crystallised orcinol dissolved in 2000 pts. of water. As the liquid is somewhat apt to froth, and the nitrosyl-solution is decomposed instantly on coming in contact with water, it is best to run it into the orcinol solution below the surface of the liquid by means of a long-necked funnel or a bulb-dropping tube furnished with a stopcock. The dinitroso-orcinol then begins to separate in a few seconds, and in the course of eighteen to twenty-four hours is completely deposited in the form of a yellowish-brown powder. For purification, it is washed with cold water; converted into an ammonium salt by suspending it while moist in 10 to 15 pts. of alcohol; adding alcoholic ammonia by small successive portions till the brown powder is completely dissolved into a green crystalline powder; finally adding a slight excess of ammonia; leaving the whole at rest for a few minutes; and separating the green crystals from the brown mother-liquor by pressure on a cloth filter. This purified ammonium salt is decomposed by stirring it up with water and dilute sulphuric acid, and leaving the mixture to itself for some hours, the dinitroso-orcinol thereby separated being collected on a vacuum-filter and well washed with cold water to remove adhering ammonium salt. Another treatment or two with alcoholic ammonia serves to remove all soluble impurities from the nitroso-orcinol, yielding a product which is of a very pale colour, but as it is liable to contain some lead sulphate derived from the concentrated sulphuric acid employed in the preparation of the nitrosyl sulphate, it is advisable to dissolve it in a dilute solution of sodium hydrate, and precipitate the filtered liquid by an acid. This is most conveniently done by suspending the purified dinitroso-orcinol in 10 to 15 pts. of water, and adding a solution of sodium hydrate until nearly the whole is dissolved. The solution is then filtered and strongly acidulated with dilute sulphuric acid.

Pure dinitroso-orcinol, prepared by the decomposition of the sodium or ammonium compound, is a pale-coloured crystalline powder, but it may be obtained in distinct crystals by adding a solution of 4 pts. of orcinol in 400 of water to a dilute aqueous solution of nitrous acid (made by pouring 20 pts. of the nitrosyl sulphate solution containing 3 of N^2O^3 into 1600 of water). The liquid becomes deep-yellow, and on standing for twenty-four hours, deposits the dinitroso-orcinol in sharply-defined transparent prisms of a deep-yellow colour. It is almost insoluble in water, alcohol, ether, benzene, &c., but dissolves in hot glacial acetic acid, and is reprecipitated apparently but little altered, on diluting the solution with water. It dissolves when boiled with alcohol, but undergoes decomposition at the same time. Cold concentrated sulphuric acid dissolves it with deep-red colour, and the solution, if at once poured into water, deposits unaltered nitroso-orcinol; on heating the solution in the concentrated acid, however, or even on allowing it to stand for some time, it is decomposed. When nitroso-orcinol is heated in a narrow tube, it begins to turn dark rapidly at 110° , but without fusing, and at 140° it becomes almost black. Heated rapidly on platinum-foil, it melts and decomposes, but without deflagration.

The potassium-, sodium-, and ammonium-derivatives of dinitroso-orcinol are green crystalline compounds, soluble in water, but only slightly soluble in alcohol. The ammonium compound is decomposed by prolonged contact with alcoholic ammonia. The derivatives containing the metals of the alkaline earths and the heavy metals are brown amorphous insoluble precipitates,



Nitro-orcinols. 1. *Mononitro-orcinols*.—An ethereal solution of orcinol treated with a mixture of nitrous and nitric acids, deposits on standing a brownish-red crystalline body, almost insoluble in ether, very sparingly soluble in alcohol, and crystallising from acetic acid in brown granular crystals with beetle-green lustre. Water containing a trace of an alkali dissolves this compound with a splendid purple colour, and the solution, when very dilute, exhibits a vermilion-red fluorescence. With concentrated sulphuric acid it forms a purple solution, which, on standing, or on heating, turns brown. The empirical formula of this body, which is not explosive, is $C^{14}H^{11}NO^3$:



On dissolving it in hot concentrated nitric acid, a dark reddish-brown liquid is formed, from which, on cooling, glistening bright-red prisms, $C^{14}H^7N^3O^{10}$, crystallise out; they dissolve in water and alcohol with a crimson colour, which turns brown on addition of ammonia. The ethereal solution, even if very dilute, exhibits a magnificent vermilion-red fluorescence.

On distilling the ethereal mother-liquor of the first of these compounds, a brown syrup is left behind, containing two mononitro-orcinols; one of them, called *α-nitro-orcinol*, volatilises with steam, and is obtained by resublimation in long, soft, glistening, orange-red needles, melting at 120° and dissolving readily in alcohol and ether, but very sparingly in cold water. On boiling it with baryta-water, the normal salt, $C^7H^3(NO^2)O^2Ba$, is obtained in bronze-coloured needles, which, when suspended in water are decomposed, the acid salt $[C^7H^3NO^2(OH)O]^2Ba$ being formed, which crystallises in small greenish-brown plates with a metallic lustre. *β-nitro-orcinol* is isolated by boiling the tarry residue left after the *α*-compound has been driven off with water, concentrating the solution, and purifying the compound, which crystallises out by boiling a dilute alcoholic solution with animal charcoal. It forms short, slender, dark lemon-yellow needles, containing 1 mol. of water and melting at 115° . The normal barium salt, $C^7H^3(NO^2)O^2Ba + 3H^2O$, forms red granular crystals, and the acid salt, $[C^7H^3NO^2(OH)O]^2Ba + 4H^2O$, crystallises in tufts of golden-yellow prisms. On adding bromine to an ethereal solution of *β*-nitro-orcinol, a compound $C^7H^3Br^2(NO^2)(OH)^2$ is obtained in dark-yellow plates, melting with decomposition at 112° . The acid barium salt contains 1 mol. of water, and crystallises in red needles. By adding iodine and mercuric oxide to an alcoholic solution of the *β*-compound, dark-yellow woolly needles of the corresponding iodine-compound are formed (Weselsky, *Ber.* vii. 439).

2. *Dinitro-orcinol*, $C^6H^4N^2O^6 = C^6H(CH^3)(NO^2)^2(OH)^2$.—Strong nitric acid acts readily on nitroso-orcinol, especially when heated, forming trinitro-orcinol, together with some oxalic acid. With dilute nitric acid in the cold, however, the action was different, dinitro-orcinol and oxalic acid being produced, but only traces of trinitro-orcinol. When finely-powdered nitroso-orcinol was added to four times its weight of nitric acid of sp. gr. 1.3, care being taken to keep the mixture cool by immersing the beaker in cold water, it gradually acquired a reddish-brown colour; the odour of nitrous fumes soon became apparent; and in the course of five or ten minutes the whole solidified to a pasty crystalline mass, which had to be stirred up at frequent intervals, to prevent its becoming warm, otherwise much trinitro-orcinol would have been formed. In this operation, it is not necessary to employ pure dry nitroso-orcinol, as the crude moist substance answers every purpose—the amount of acid being adjusted so that for every 100 pts. of orcinol originally taken, about 550 of the nitric acid shall be employed. After standing for twenty to twenty-four hours, the product, which had become of an orange colour, was mixed with an equal bulk of cold water, collected on a vacuum-filter, and well washed with cold water. The dry product was then dissolved by agitation with cold ether, in which it is readily soluble; the solution filtered and evaporated to dryness in the water-bath; and the dinitro-orcinol was finally purified by two or three crystallisations from boiling spirit.

Dinitro-orcinol crystallises in deep yellow rhomboidal plates, which are almost insoluble in cold water, more soluble in boiling water, but crystallises out again almost entirely on cooling. It is very soluble in ether, and requires about 18 pts. of alcohol at 15° for solution. It is also slightly soluble in carbon bisulphide, and readily in hot benzene, but almost insoluble in light petroleum. Dinitro-orcinol melts at 164.5° , two degrees higher than trinitro-orcinol, but, unlike the latter, which explodes a little above its melting point, dinitro-orcinol may be heated to above 190° without alteration, and with care may even be sublimed at a somewhat higher temperature. Heated rapidly on platinum foil, it fuses and deflagrates. It is slightly soluble in strong sulphuric acid, with a yellow colour, but when heated with the acid, it dissolves with effervescence, forming a deep orange-coloured solution,

which does not yield a precipitate on the addition of water. It dissolves in hot concentrated nitric acid, and is at the same time converted into trinitro-orcinol.

The derivatives which dinitro-orcinol forms with the alkali-metals, as also the corresponding ammonium-compound, are very soluble in water, and difficult to obtain in the crystalline state; they are of an orange-red colour. When dinitro-orcinol is boiled with water and silver oxide or carbonate, it is decomposed, the silver being reduced, and forming a metallic mirror on the side of the vessel. With barium, it forms two compounds, one of which is almost insoluble in water, and of a deep crimson colour; the other, which forms long silky needles of a bright yellow colour, is sparingly soluble in boiling water, but crystallises out almost entirely on cooling. The crimson barium compound may be obtained by adding an excess of an aqueous solution of barium hydrate to a solution of dinitro-orcinol in spirit: on boiling the mixture, the salt is thrown down as a crystalline powder. It dissolves on boiling it with water and excess of dinitro-orcinol, and the solution, on cooling, deposits the acid salt in orange-yellow needles. In order to obtain them free from dinitro-orcinol, however, it is best to operate in the following manner:—2 pts. of dinitro-orcinol are dissolved in 40 of alcohol, and the solution divided into two parts, one of which is slightly less than the other. The smaller portion is then heated, diluted with its own bulk of hot water, and boiled; a cold saturated aqueous solution of barium hydrate is now added in slight excess (a quantity rather more than equal in volume to the solution of dinitro-orcinol in alcohol and water); the mixture is left to cool in a closed vessel to prevent formation of barium carbonate by absorption of carbonic anhydride from the air; and the precipitate is collected on a vacuum filter and thoroughly washed with cold water. The crimson basic salt thus obtained is converted into the acid salt by boiling it with a considerable quantity of distilled water, and adding the second larger portion of the alcoholic solution of dinitro-orcinol. The crimson salt soon dissolves, and the clear liquid, on cooling, solidifies to a mass of the needle-shaped crystals of the acid barium salt; a second crystallisation from boiling water suffices to purify it. Determinations of the amount of barium gave 23.69 per cent. and 23.61 per cent. Ba, agreeing with the formula $[C^6H^4(NO_2)_2OH]^2BaO^2 + H^2O$ (Stenhouse a. Groves, *loc. cit.*)

3. *Trinitro-orcinol*, $C^6H^3N^3O^8 = C^6(CH^3)(NO_2)^3(OH)^2$, may be prepared by heating orcinol at 100° with excess of sulphuric acid, treating the resulting sulphonic acid after cooling, first with dilute, then with concentrated, and finally with fuming nitric acid in excess, and pouring the product into cold water (Merz a. Zetter, *Ber. xii.* 681).

Aldehydes from Orcinol, and their Derivatives (Tiemann a. Helkenberg, *Ber. xii.* 999). When a solution of orcinol in very dilute soda is boiled with chloroform, three aldehydes are formed, which may be separated by acidifying the mixture with sulphuric acid, and distilling in steam, when *α-orcendialdehyde* will be found in the distillate. By extracting the residue in the retort with ether, a mixture of *orcylaldehyde* and *β-orcendialdehyde* is obtained, from which the latter is removed by shaking up the ethereal extract with a solution of sodium-hydrogen sulphite.

Orcylaldehyde, $C^6H^2(CH^3)(OH)^2.CO.H$.—The crude product is purified by solution in potash, and reprecipitation by acids; it is then recrystallised from benzene, and finally from water. The pure substance forms colourless needles (m. p. 177°), which dissolve freely in alcohol, ether, chloroform, hot benzene, and boiling water. It unites with aniline to form *orcylaldehydianilide*, $C^6H^2(CH^3)(OH)^2.C(N.C^6H^5)H$, which crystallises in yellow prisms (m. p. 125°), soluble in alcohol, ether and chloroform.

Homoacetoxycoumarin, $CH^3(OC^2H^3O)C^6H^2 < \begin{smallmatrix} O \\ CH=CH \end{smallmatrix} > CO$, obtained by the action of acetic anhydride and sodium acetate on *orcylaldehyde*, crystallises in colourless needles (m. p. 126°), which are soluble in alcohol and ether. This compound gives a blue coloration with alkalis.

α-Orcendialdehyde, $C^6H(CH^3)(OH)^2(COH)^2$, forms long needle-shaped crystals (m. p. 117°), soluble in alcohol, ether, chloroform, and in hot water. This aldehyde unites with aniline, forming *α-orcendialdehydedianilide*, $C^6H(CH^3)(OH)^2[C(N.C^6H^5)H]^2$, a yellow crystalline powder, which melts at 281° .

β-Orcendialdehyde is obtained in pale yellow crystals by decomposing its sodium-sulphite compound with sulphuric acid, extracting with ether, and recrystallising from benzene and from dilute alcohol. This substance melts at 168° , but sublimes at a lower temperature. It is soluble in alcohol, ether, chloroform, benzene, and hot water.

Isorcetnols. Two compounds isomeric with orcinol, and distinguished as *α*- and

γ -isoreinols, are produced, by the action of melting potassium hydroxide on the respective toluenesulphonic acids (*q. v.*)

a-Isoreincol, obtained in this manner, together with salicylic acid and slight traces of paraoxybenzoic acid, from *a*-toluenedisulphonic acid, crystallises from water in thickly felted groups of small needles containing water of crystallisation and melting at about 95° . In the anhydrous state it melts at 87° – 88° , boils at about 270° , and yields by distillation a thick liquid which takes a long time to solidify. *a*-Isoreincol is not altered by exposure to the air. With ferric chloride and with silver nitrate and ammonia it produces a violet-blue coloration, which soon disappears. It is coloured yellow by chloride of lime, and blue by contact with ammonia and moist air. By fusion with sodium formate, it yields a dicarboxylic acid which forms sparingly soluble white flocks exhibiting signs of fusion below 270° (Hakansson, *Ber. v.* 1087).

γ -Isoreincol is formed, also together with salicylic acid, by fusing γ -toluenedisulphonic acid with potassium hydroxide and a little water. On acidifying the aqueous solution of the melt with sulphuric acid, agitating with ether, and treating the resulting ethereal solution with sodium carbonate, the salicylic acid is removed, while the isoreincol remains in the ethereal solution, and may be separated by precipitating with basic lead acetate, and decomposing the precipitate with hydrogen sulphide. It forms a radio-crystalline mass, containing 1 mol. water which is given off at 100° . It differs considerably from orcinol in its properties and reactions, has a sweet but not nauseous taste, melts at 87° and boils at 260° . It dissolves in water, alcohol, and ether; the aqueous solution, syrupy at first, soon solidifies throughout the entire mass. It does not change colour in contact with the air; produces a brownish-green colour with ferric chloride, and a black precipitate with ammoniacal silver solution; is coloured red and gradually yellow by chloride of lime; and when exposed to moist air in contact with ammonia, acquires a brownish colour, which is removed by acetic acid (Senhofer, *Liebig's Annalen*, clxiv. 126).

Betoreincol, $C^6H^{10}O^2 = C^6(CH^3)^2H^2(OH)^2$. This homologue of orcinol, obtained by the destructive distillation of the lichen, *Usnea barbata*, was discovered in 1848 by Stenhouse (*iv.* 214)—who named it *B-orcin*—and has lately been further investigated by Stenhouse & Groves (*Chem. Soc. J.* xxxvii. 366), the name being changed, in accordance with present usage, to *Betoreincol*.* It was originally regarded as a product of the decomposition of usnic acid, but recent experiments have shown that pure usnic acid does not yield a trace of it, and that it must therefore be produced from some other constituent of the lichen; this constituent has, in fact, been isolated, and will be described further on.

To prepare betoreincol, *Usnea barbata*, carefully freed from other lichens, is exhausted with milk of lime, the solution precipitated by hydrochloric acid, and the precipitate boiled with lime and water. The clear solution is neutralised with hydrochloric acid and evaporated, whereupon the crude betoreincol crystallises out. When purified by crystallisation from benzene and from water it melts at 163° . It is less soluble than orcinol; gives a bright crimson colour with hypochlorites, orcinol giving a purplish red; and its ammoniacal solution is rapidly coloured on exposure to air, whereas the corresponding orcinol solution is but slowly changed thereby.

Chlorobetoreincols. *Tetrachlorobetoreincol*, $C^6H^8Cl^4O^2 = C^6(CH^3)^2Cl^2(OCl)^2$, is obtained by the action of chlorine in excess on betoreincol, the best mode of preparation being to add a solution of betoreincol to a solution of chlorine hydrate. A mixture of crystalline chlorine hydrate is first prepared by passing a current of chlorine, with occasional agitation, through water to which about one-fourth part of crushed ice has been added; betoreincol is then dissolved in 50 parts of boiling water; the cooled solution is gradually added to a portion of the chlorine hydrate mixture, leaving the latter in slight excess, and the colourless mixture is left to itself for twelve to twenty hours: it then deposits the tetrachlorinated compound in colourless crystals which may be purified by one or two crystallisations from light petroleum. This compound forms large white prismatic crystals which melt at 109° , and are easily soluble in benzene, but insoluble in water.

Dichlorobetoreincol, $C^6H^8Cl^2O^2 = C^6(CH^3)^2Cl(OH)^2$, is obtained by the action of reducing agents on the tetrachloro-compound just described. The best mode of preparation is to add the tetrachloro-compound by small portions to a solution of hydriodic acid containing 15 per cent. iodine and a small quantity of red phosphorus, in a flask with reversed condenser, taking care that each portion of the tetrachloro-compound is reduced before the next is added, and continuing the boiling, till the last portions are reduced and the whole assumes the appearance of a mass of slender

* *B-orcinol* would signify an isomeride rather than a homologue of orcinol.

colourless needles. The dichlorobetorcinol thus obtained forms, after washing and recrystallisation from light petroleum, long colourless needles which melt at 142° and dissolve in carbon bisulphide, benzene, and ether.

Bromobetorcinols. The *tetrabromo-compound*, $C^6H^2Br^4O^2 = C^6(CH^3)_2Br^2(OBr)^2$, may be prepared by adding betorcinol to bromine and water, keeping the bromine in excess, or better by pouring a mixture of 5 pts. bromine and 30 pts. by measure of carbon sulphide on 1 pt. of finely powdered betorcinol, and gently heating the mixture in a flask furnished with a condensing tube. As soon as the whole of the betorcinol is dissolved, the dark brown solution is decanted from traces of black tar and agitated with an equal bulk of warm water, whereupon the colour gradually becomes lighter; if it should disappear entirely, more bromine must be added. The solution of tetrabromobetorcinol in carbon sulphide is then separated from the supernatant liquid, concentrated by distillation, and left to evaporate, and the crystals which form are purified by recrystallisation from light petroleum. A very pure product may be at once obtained by acting on pure colourless dibromobetorcinol with bromine and water at a gentle heat, and crystallising the product from carbon sulphide and light petroleum.

Tetrabromobetorcinol crystallises in large colourless prisms melting at 101° , and very similar in appearance to the tetrachloro-compound. It is very soluble in ether, benzene, and carbon sulphide, less so in petroleum.

Dibromobetorcinol, $C^6H^2Br^2O^2 = C^6(CH^3)_2Br^2(OH)^2$, may be prepared, like the corresponding chlorine-derivative, by reducing the tetrabromo-compound with hydriodic acid and red phosphorus, taking care that the reduction does not go too far: much more conveniently however by treating betorcinol with bromine diluted with carbon sulphide, the action then going no further than the production of the dibromo-derivative, since the presence of water is necessary to convert this compound into tetrabromo-betorcinol. The resulting solution concentrated by distillation yields the dibromo-compound in nearly colourless crystals, which may be purified by washing with a little carbon sulphide and recrystallisation from light petroleum. Dibromobetorcinol forms long needles melting at 155° , and closely resembling the dichloro-derivative.

The fact that the action of bromine on betorcinol when water is carefully excluded displaces only two atoms of hydrogen, whereas, in presence of water, a tetrabromo-derivative is formed, is due to the great difference between the amount of energy involved in the formation of gaseous hydrogen bromide by the direct union of bromine and hydrogen, and that which is manifested in the formation of hydrobromic acid in aqueous solution, the quantities of heat evolved in the two cases being, according to Thomsen (vii. 612), $H + Br = 8440$, and $H + Br + aq. = 28376$ gram-degrees. Now in betorcinol the two H-atoms united with carbon in the benzene-nucleus are displaced by bromine with comparative facility, the compound $C^6(CH^3)_2Br^2(OH)^2$ being produced, with evolution of HBr ; but in the case of the two H-atoms united with oxygen in the OH -groups, it is only when the much greater energy involved in the formation of hydrobromic acid in presence of water is exerted, that substitution takes place, resulting in the formation of the tetrabromo-derivative. A precisely similar difference is observed in the action of bromine on orcinol, accordingly as water is present or absent, the substitution in the latter case going no further than the production of tribromorcinol.

Iodobetorcinol, $C^6H^2IO^2 = C^6(CH^3)_2HI(OH)^2$. This compound, the only known iodo-derivative of betorcinol, may be prepared similarly to iodorcinol (vii. 879) by the action of lead oxide on betorcinol and iodine in ethereal solution. After crystallisation from light petroleum, it melts at 93° . It dissolves very readily in ether, benzene, and carbon sulphide, very sparingly in boiling water, more freely in dilute spirit, but does not crystallise well from the latter.

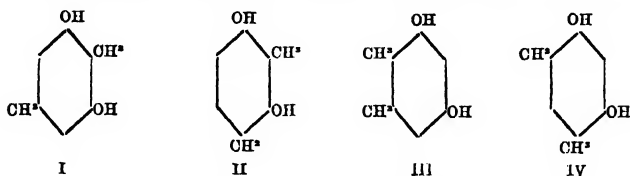
Nitrosobetorcinol, $C^6H^2NO^2 = C^6(CH^3)_2H(NO)(OH)^2$, is readily prepared by the action of nitrosyl sulphate, $SO^2(NO)OH$ (p. 1419) on betorcinol in aqueous solution. Betorcinol (2 pts.) is dissolved in 100 pts. of boiling water, and the solution, after filtering and cooling, is poured into a mixture of 7 pts. nitrosyl sulphate solution (containing 15 per cent. N^2O^3) with 200 pts. of water, whereupon a brilliant orange-red precipitate makes its appearance. This, after a few minutes, is collected on a vacuum-filter, washed by stirring it up with 100 pts. of water, and again collecting, repeating the washing once more in the same manner so as to remove the last trace of free acid, and finally dried at a gentle heat.

Nitrosobetorcinol is moderately soluble in water and readily in alcohol, but is not easily recovered from either of these solvents in the crystalline state. It dissolves very readily in hot glacial acetic acid, and separates on cooling in small bright-red prismatic crystals. It is sparingly soluble in light petroleum and in carbon sulphide,

somewhat more freely in hot benzene, from which it crystallises on cooling; easily soluble in ether.

This compound, in which only one of the hydrogen-atoms is replaced by NO, appears to be the only nitroso-derivative of betorcinol, whereas orcinol and resorcinol, when treated with nitrous acid, yield dinitroso-derivatives. Considering now that the action of nitrous acid on phenol, the *monhydroxy*-derivative of benzene, gives rise to a *mononitroso*-phenol in which the NO-group occupies the para-position with respect to the OH-group, and that, of the three *metadihydroxy*-derivatives of phenol, resorcinol and orcinol yield *di*-nitroso-derivatives, whilst betorcinol yields only a *mononitroso*-derivative, it seems not improbable that, in the latter, the para-position with respect to one of the OH-groups is occupied by a CH³-group.

Of the four possible formulæ for betorcinol, or *dimethyl-dihydroxybenzene*, viz.



I. is capable of yielding a dinitroso-derivative in which the NO-groups can occupy a para-position with respect to the OH-groups, and in IV. the para-positions are occupied by CH³-groups, so that it could not yield a nitroso-derivative of this class, whilst in II. and III. there is *only one* para-position into which the NO-group could enter, whence it follows that these bodies would yield *mononitroso*-derivatives. Our knowledge of the laws which govern the introduction of the nitrosyl-group into the hydroxyl-derivatives of benzene is at present far too limited to enable us to pronounce with certainty on this point; but it seems most probable that the constitution of betorcinol is represented by the formula II. or III. rather than by I. or IV.

The acid which yields betorcinol may be separated from usnic acid by means of its greater solubility in cold ether. It melts at 186°, and decomposes at a somewhat higher temperature, yielding carbon dioxide and betorcinol. It is represented by the formula C¹²H¹⁰O⁷, and is related to betorcinol in the same manner as evernic acid, C¹⁷H¹⁶O⁷, to orcinol, and might therefore be regarded as *dimethyl-evernic acid*. As however this constitution cannot at present be assigned to it with certainty, Stenhouse & Groves have provisionally named it *barbatic acid*. Hesse (*Ber. x.* 1326) obtained from an *usnea* growing on Calisaya bark, an acid which he called *usnetic acid*. This acid is probably not identical with barbatic acid, but may be an ethereal salt thereof, as alcohol was used in its extraction and purification.

ORCINOL-PETHALEIN. See PHTHALEINS.

ORGANIC COMPOUNDS. *Decomposition of Organic Liquids by the Electric Spark.*—Berthelot inferred from his experiments on the action of a red heat on hydrocarbons (vi. 259), that when a hydrocarbon of high molecular weight is submitted to destructive distillation, the four fundamental hydrocarbons, acetylene, ethylene, methane, and ethane are first separated, and these, immediately entering into combination with each other, produce the more complex hydrocarbons which are actually obtained; and this view has been considerably strengthened by the recent experiments of Truchot (*Compt. rend. lxxxiv.* 714), in which organic compounds were decomposed in such a manner that the simpler hydrocarbons produced in the first instance were prevented from recombining, and thus obtained in the free state. This was effected by passing a powerful induction spark through the liquid itself, and collecting the resulting gases.

Volatile liquids, such as pentane, pentylene, and ethyl oxide thus treated give about 1 litre of gas per hour, but compounds of higher boiling point give considerably less. The gas invariably contains hydrogen in addition to the hydrocarbons already mentioned, but no compound containing more than two atoms of carbon in the molecule is present. With the liquid paraffins, no deposit of carbon occurs during the decomposition, provided the liquid be kept slightly warm; and a trace of carbon only is obtained in the case of an olefine. With the less saturated hydrocarbons, however, such as the terpenes and benzene derivatives, a tolerably abundant deposition of carbon always takes place. Compounds containing oxygen, such as alcohol, ether, and

the aldehydes, give no carbon; but, in addition to the fundamental hydrocarbons, they evolve carbon monoxide, unaccompanied by carbon dioxide or water-vapour.

Action of Boron Fluoride.—The action of this compound on hydrocarbons and oxygenated organic bodies has been studied by F. Landolph (*Ber.* x. 1312). By passing the gas over comminuted *camphor*, a crystalline mass is obtained which melts below 200° , gives off the whole of the absorbed gas on distillation, leaving the camphor in the pure state, but when heated to 250° in a sealed tube for 24 hours is completely resolved into boric acid, gases having an acid reaction, and a mixture of hydrocarbons, the chief constituent of which (amounting to 40 per cent. of the camphor decomposed) is *cy mène*. At the same time there is formed a yellowish-green viscid hydrocarbon which boils above 350° .

Anisöl is violently attacked by boron fluoride, yielding a body which distils over at 158° – 163° , and hydrocarbons of high boiling point, together with a heavy liquid which is partially decomposed by contact with the air, with separation of boric acid, and is resolved by water into boric acid and hydrogen fluoride.

With *benzaldehyde*, boron fluoride unites in definite proportions, forming a well-crystallised compound, which on exposure to the air splits up into benzaldehyde, boric acid, and hydrogen fluoride, and when heated to 250° in a sealed tube for 24 hours, is converted into a black solid mass from which ether extracts a hard white substance melting at 123° – 124° , solidifying again at 80° , and crystallising from water in slender shining needles.

Chloral is converted by boron fluoride into metachloral; acetic acid into the anhydride; succinic acid is not acted on. With *ethylene*, boron fluoride forms ethylene fluoboride, a liquid which boils at 126° , and when exposed to the air immediately evaporates, giving off white strongly acid fumes, together with ethylene, and leaving a small quantity of boric acid.

Action of Chromyl Chloride, CrO_2Cl_2 (Etard, *Compt. rend.* lxxxiv. 127; *Bull. Soc. Chim.* [2], xxvii. 249). 1. *Chloroform* treated with this compound yields carbonyl chloride, COCl_2 . 2. *Glacial acetic acid* heated to 100° in sealed tubes with chromyl chloride yields a cry. 'alline salt, $\text{Cr}^2\text{O}^+[\text{Cr}^2(\text{C}^2\text{H}^3\text{O}^2)]^2 + 8\text{H}^2\text{O}$, which exhibits dichroism (being yellow-green by transmitted, dark green by reflected light), together with free chlorine and chromic chloride; no acetyl chloride was observed. 3. *Ethyl acetate* is converted into acetic acid and aldehyde. 4. *Pentane* from petroleum and *inactive amyl chloride* yields chloromethyl-isobutyl ketone, $\text{CH}^2\text{Cl}-\text{CO}-\text{CH}^2.\text{CH}(\text{CH}^3)_2$, a colourless liquid having a pungent aromatic odour, and boiling without decomposition at about 120° . 5. *Hexane* is converted into an acid, and a liquid, $\text{C}^6\text{H}^{11}\text{ClO}$ (probably a chlorinated ketone), which boils at 145° – 150° , easily reduces ammoniacal silver solution, does not unite with acid sodium sulphite, and is not attacked by potassium hydrate. 6. *Benzene* is converted into quinone. 7. *Paradibromobenzene* yields a compound, probably $\text{C}^6\text{Cl}^2\text{Br}^2\text{O}^2$, converted by soda-ley into chloranilic acid. 8. *Nitrobenzene* yields nitroquinone, $\text{C}^6\text{H}^2(\text{NO}^2)_2\text{O}^2$, which crystallises in yellow shining scales, melts at 232° , and sublimes at a higher temperature. 9. *Phenol* yields quinolic ether, $\text{C}^6\text{H}(\text{OH}).\text{O}.\text{C}^6\text{H}(\text{OH})$, a white uncrystallisable substance convertible by oxidation into quinone. 10. *Toluene* yields benzaldehyde, together with benzyl chloride. 11. Nitrotoluene is converted into nitrotoluquinone, $\text{C}^6\text{H}^2(\text{NO}^2)(\text{CH}^3)\text{O}^2$, which forms large brown-yellow crystals melting at 237° , and easily subliming. The reaction is attended with the formation of a somewhat considerable quantity of ozone (Etard).

Anthracene dissolved in acetic acid is converted by chromyl chloride into anthraquinone (Haller, *Ber.* x. 734).

Analysis.—A method of determining the carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, and halogen elements in an organic compound by a single combustion is described by A. Mitscherlich (*Ber.* vi. 1000). It consists in burning the substance with mercuric oxide in a combustion-tube from which the air has been displaced by a current of pure nitrogen, the mercuric oxide in contact with organic matter being reduced at a temperature below that which is required for its decomposition by heat alone. The water and carbon dioxide thereby formed are estimated by absorption and weighing in the usual manner; the mercury reduced by the combustion is driven by a strong stream of nitrogen into a weighed tube; and the quantity of oxygen equivalent to this reduced mercury, deducted from the total amount of oxygen contained in the carbon dioxide and water together, gives the quantity of that element contained in the substance under examination. *Chlorine, bromine, or iodine*, if present, unites with a portion of the liberated mercury, forming a compound which passes over with the metallic mercury, and may be estimated by weighing. *Sulphur and phosphorus* are oxidised to sulphuric and phosphoric acid respectively, which may be esti-

mated by known methods. *Nitrogen-compounds* yield nitrogen dioxide, which may be absorbed by a mixture of chromic acid and stannous chloride in an apparatus placed between the calcium chloride tube and the potash-bulbs.

A similar method for the simultaneous determination of carbon, hydrogen, nitrogen, and oxygen is given by Frerichs (*Ber.* x. 26). The substance is burned with mercuric oxide in a tube exhausted of air, and the evolved gases are dried, passed into a eudiometer, and analysed in the usual way. The water formed is absorbed by phosphoric anhydride.

A method of analysis by *reduction*, whereby the carbon, hydrogen, and oxygen in an organic compound may be determined directly, is described by H. Cretier (*Zeitschr. anal. Chem.* 1874, 1). The vapour of the organic body or of its products of decomposition is passed over ignited magnesium-powder, which abstracts the whole of the oxygen, yielding a gaseous mixture consisting only of carbon and hydrogen, in which these elements can be estimated by the usual methods of gas-analysis. In this manner the entire weight of hydrogen in the organic substance is at once obtained; and that of the carbon may be ascertained by adding the weight of the charcoal remaining after the decomposition to that contained in the gaseous mixture. The amount of oxygen is calculated from the weight of the unaltered magnesium. The results, however, are not very exact.

On the estimation of *Chlorine, Bromine, and Iodine* in Organic Compounds, see HALOGENS (p. 924).

To obviate the errors arising from the use of reduced copper for decomposing the nitrogen oxides evolved in the combustion of azotised organic bodies (p. 183), Perkin has devised a method of removing these compounds by oxidation and absorption, instead of reducing them with copper. The best absorbent for the purpose is a mixture of potassium chromate and manganese dioxide. In making a combustion, about 6 inches of the mixture are placed in the front part of the tube (the oxygen process being used) and the whole of the tube is heated and dried with air in the usual way. The temperature of the mixture is then allowed to fall to about 200° to 250°, and the combustion is conducted in the ordinary way. By re-heating the mixture strongly and passing a current of air over it, the oxides of nitrogen are removed and the mixture is ready for a second combustion. If the organic substance contains sulphur, a greater length of the mixture must be used, the back part being strongly heated to absorb the sulphur dioxide, and the front part maintained at 200° to 250° to absorb the oxides of nitrogen (*Chem. Soc. J.*, 1880, xxxvii. 121, 418).

An indirect method for the quantitative analysis of a mixture of organic compounds of known composition, by means of equations with several unknown quantities, is proposed by R. Popper (*Zeitschr. anal. Chem.* x. 429). An ultimate analysis of the mixture is first made, and the resulting equation, $x + y + z + \dots = v$, is combined with those which are deduced from the percentages of carbon and hydrogen in the several proximate constituents of the mixture. Suppose, for example, that a mixture of stearic acid, naphthalene, and pyrocatechin, weighing 0.555 grams, gives by ultimate analysis 0.3936 carbon and 0.0422 hydrogen: then we have the three equations:

$$\begin{aligned} x + y + z &= 0.555 \\ \frac{216}{284}x + \frac{120}{128}y + \frac{72}{110}z &= 0.3936 \\ \frac{36}{284}x + \frac{8}{128}y + \frac{6}{110}z &= 0.0422 \end{aligned}$$

in which the denominators are the molecular weights of the three constituents, and the numerators are the atomic weights of the quantities of carbon and hydrogen contained therein.

On the estimation of Organic Matter in Potable Waters, see Dittmar & Robinson (*Chem. News*, xxxvi. 26; *Chem. Soc. J.* xxxii. 806).

On the Incineration of Organic Matter preparatory to testing for Metallic Poisons, see Verryken (*Chem. Centr.* 1873, 696; *Chem. Soc. J.* xxvii. 603).

On Incineration with Barium or Potassium Hydrate for the estimation of Chlorine and Alkalis, see Behagel von Adlerskron (*Zeitschr. anal. Chem.* 1873, 390; *Jahresb. f. Chem.* 1873, 949).

ORGANOIDS. The organoids of the peninsula of Abscheron on the Caspian Sea have been described by H. Abich (*N. Petersb. Acad. Bull.* xxi. 493). The petroleum has lately been obtained in this locality by numerous borings, and rises in the bore-holes under very high pressure. In one shaft near Balachani, Abich found a brownish layer resembling sandstone, covered with alluvial argillaceous sands, con-

taining numerous concretions in its lower part, and gradually passing into true sandstone. An analysis of the mass by C. Schmidt gave:

X (%)	NaCl	K ² SO ⁴	Na ² SO ⁴	CaSO ⁴	MgSO ⁴	CaCO ³	Y (%)	Z (%)
10.150	0.011	0.008	0.034	0.126	0.053	9.382	33.059	47.177 = 100

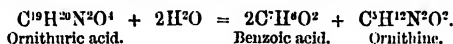
(*) Volatile matters, of which 1.630 per cent. consisted of water and other matters given off at 100°, 0.793 per cent. at 100°-110°, and 7.687 per cent. above 110°. (†) Silicates, and silica soluble in hydrofluoric acid. (‡) Quartz-sand insoluble in hydrofluoric acid.

The silicates included under Y consisted for the most part of:

SiO ²	Al ² O ³	Fe ² O ³	Mn ² O ³	MgO	CaO	Na ² O	K ² O
29.405	1.799	0.529	0.005	0.345	0.223	0.429	0.324 = 33.059

According to these results, the rock is a mixture of about 10.1 per cent. naphtha and paraffin, 0.3 sea-salts, 0.4 fragments of shells, 10.4 felspar with a little mica, and 68.8 quartz-sand.

ORNITHINE, C³H¹²N²O² (Jaffe, *Ber.* x, 1925). A base obtained by prolonged boiling of ornithuric acid (*infra*) with hydrochloric acid:



It has not yet been obtained quite pure, but it forms well-crystallised salts with acids. Two *hydrochlorides* have been obtained, viz. 3C³H¹²N²O².2HCl and C³H¹²N²O².HCl; also an *oxalate* probably having the composition 3C³H¹²N²O².2C²H²O⁴. Ornithine is regarded by Jaffe as diamidovaleric acid, C⁴H¹⁷(NH²)².CO²H.

Benzoyl-ornithine, C¹¹H¹⁴(C⁷H⁸O)N²O², is obtained by boiling ornithuric acid with hydrochloric acid until the whole is just dissolved. It crystallises in hard colourless needles; melts at 225°-230°; dissolves readily in water, but is insoluble in alcohol and in *ether*; reacts with acids, forming easily soluble salts. By prolonged boiling with hydrochloric acid it is resolved into benzoic acid and ornithine.

ORNITHURIC ACID, C¹⁰H²⁰N²O⁴ (Jaffe, *loc. cit.*) An acid formed by the decomposition of benzoic acid in the organism of birds. It is extracted from the excrements of birds whose food has been mixed with benzoic acid, by boiling with alcohol, evaporating the filtrate, redissolving the residue in absolute alcohol, and again evaporating the filtered solution. The residue which then remains is mixed with a small quantity of water and shaken up with ether, which dissolves fat, benzoic acid and ornithuric acid (because it is still impure); the ethereal solution is decanted, and the residue is mixed with dilute sulphuric acid and again shaken up with ether. The united ethereal solutions, left at rest in a cool place, deposit ornithuric acid only slightly coloured. The greasy mass left undissolved by the ether is set aside to crystallise; the solidified crystalline mass is left to drain on a filter, then washed on the filter with water, and dissolved in hot water and ammonia; the solution boiled with milk of lime and filtered; the strongly coloured filtrate cautiously decolourised by small quantities of potassium permanganate; and the clear nearly colourless filtrate is mixed with hydrochloric acid, whereupon it deposits ornithuric acid. For further purification, the united products are repeatedly crystallised from alcohol.

Ornithuric acid crystallises in small colourless anhydrous needles; melts at 182°; is nearly insoluble in ether, sparingly soluble in water, more freely in ethyl acetate, most easily in hot alcohol. When somewhat strongly heated, it gives off an odour of bitter almonds and yields a woolly sublimate. It reddens litmus, forms soluble salts with the alkalis and alkaline earths, insoluble salts with the oxides of the heavy metals. Its decomposition by hot hydrochloric acid has been already mentioned.

In constitution ornithuric acid is analogous to hippuric acid, being formed by the union of 2 mol. benzoic acid and 1 mol. ornithine, with elimination of 2 mol. water.

OROSELONE, C¹⁴H¹²O⁴. See PEUCEDANIN.

ORTHITE. This mineral has been found, together with albite, in a trachyte-enclosure of the trachytic conglomerate of the Langenberg, near Heisterbach, in the Siebengebirge. This is the third instance of the occurrence of orthite—formerly known only as belonging to the palaeocrystalline rocks (iv. 237)—in volcanic rocks, the other two volcanic localities in which it has been found being Laach in the Eifel and Vesuvius (G. vom Rath, *Pogg. Ann. Jubelb.* 1874, 547).

From numerous analyses of orthite from various localities, Engström (*Ber.* x, 1727) deduces the formula 2(2RO.SiO²) + 3RO².4SiO², with 1 or with 2H²O, regarding the first, viz. Si²R²R²H²O²⁰, which is analogous to the formula of epidote (p. 736), as the true formula of undecomposed orthite.

On the microscopic characters of orthite, allanite, and gadolinite, see Sjögvén (*Jahrb. f. Min.* 1877, 730; *Chem. Soc. J.* xxiv. 387).

ORTHOCLASE. Well-defined orthoclase crystals from a granite cleft at Schiltach in Baden, are described by F. Klocke (*Jahrb. f. Min.* 1874, 868). They belong partly to the ordinary type $\infty P. \infty P\infty. 0P. P\infty$, partly to the rarer type, $\infty P. \infty P\infty. 0P. P\infty$. Some of the crystals exhibit also the well-known occurrence of implanted crystals of albite. Westphal (*ibid.* 33) found orthoclase crystals resembling sanidin in a vein of porphyry near Weistropp between Dresden and Meissen. C. Doelter (*Min. Mitth.* 1875, 180) describes orthoclase in simple crystals and in Carlsbad twins, from the quartz-porphyry of the Val di Madonna, a side valley of the Val Floriania on the north-west declivity of the Zocchialti mountain, South Tyrol. A fine pseudomorphous penetration-twin crystal of tin-stone after orthoclase, from Redruth, Cornwall, has been examined by H. Laspeyres (*Jahrb. f. Min.* 1877, 529) who finds the twin law to be one entirely new to orthoclase, viz.: 'the twin-plane a face of ∞P .' The two halves of this penetration-twin are extremely well developed contact-twins according to the Carlsbad law, viz.: 'the two individuals of each Carlsbad-twin being a right and left crystal.'

The following are recent analyses of orthoclase: 1. From Greenland granite (Kottal, *Wien. Akad. Ber.* [1], lxi. 94). 2-4. From the granitic gneiss of New York. 2. Colourless, translucent, distinctly cleavable; 3. Flesh-coloured, indistinctly cleavable, enclosing numerous crystals of mica; 4. Of medium purity and colour (P. Schweitzer, *Amer. Chem.* iv. 444):

SiO ²	Al ² O ³	Fe ² O ³	K ² O	Na ² O	H ² O	Sp. gr.
65.00	17.85	0.28	15.75	0.83	— = 99.71	2.57
64.99	18.55	0.64	12.24	3.48	0.13 = 100.03	2.559
65.47	18.22	0.67	13.71	2.21	0.19 = 100.47	2.562
65.50	17.94	0.87	13.11	2.40	0.23 = 100.05	2.558

A sodium felspar with orthoclastic cleavage, allied, therefore, to loxoclase, occurs in the slugs and tufas of the island of Rachgoun, Algeria. See LOXOCLASE (p. 1242). For other analyses of orthoclase, see FELSPAR (p. 773).

ORTHO-DERIVATIVES, AROMATIC. *Ortho-acetobromanilide* and *-chloranilide*. See ACETAMIDES (pp. 4, 5).

Ortho-aldehydo-salicylic Acid. See BENZOIC ACIDS (Oxy-), (p. 288).

Ortho-aldehydo-vanillic Acid. See BENZOIC ACIDS (Dioxy-), (p. 292).

Ortho-amidodibromobenzenesulphonic Acid, C⁶H³(SO²H)(NH²).Br.H.Br.H. On the reaction of this acid with bromine, see BENZENESULPHONIC ACIDS (p. 231).

Ortho-amidodiphenyl. See PHENYL (Di-).

Ortho-amidophenolsulphonic Acid. See PHENOLSULPHONIC ACIDS.

Ortho-amidosalicylic Acid. See BENZOIC ACIDS (Oxy-), (p. 283).

Ortho-benzenedisulphonic Acid, or *Benzen-orthodisulphonic Acid*, C⁶H⁴(SO²H)(SO²H). This acid is formed by boiling metadiazobenzenesulphonic acid with alcohol. Its *chloride*, C⁶H⁴(SO²Cl)², crystallises in large colourless four-sided plates, melting at 105°; the *amide*, C⁶H⁴(SO²NH²)², in small needles, separate or grouped in nodules, and melting at 233°. The following is a comparison of the melting points of the chlorides and amides of the three benzenedisulphonic acids (compare p. 257):

	Ortho	Meta	Para
Chloride	105°	63°	132°
Amide	233	229	288

(Drebes, *Ber.* ix. 553; compare table, p. 257).

Ortho-cresol. See PHENOLS.

Orthodiazobenzoic Nitrate. See BENZOIC ACIDS (DIAZO-), (p. 274).

Orthonitranilinesulphonic Acid, C⁶H⁴(NO²)(NH²)(SO²H), is formed by heating orthonitrobenzanilide (m. p. 94°) with pyrosulphuric acid on the water-bath for several hours. The free acid and its barium salt, [C⁶H⁴(NO²)(NH²)SO²]²Ba + H²O, crystallise in thick yellow needles (Behrens a. Post, *Ber.* viii. 1558).

Orthonitrobenzamidril, C⁶H⁴NO².CN, [NO²: CN = 1: 2], is obtained by heating orthonitrobenzamide (m. p. 174°) with phosphoric anhydride to 180°. It crystallises in needles easily soluble in water and alcohol, and melting at 109° (Hübner a. Bärthlein, *Ber.* x. 1713).

On *Meta-* and *Paranitrobenzonitril*, see p. 307.

Orthonitrobenzyl Chloride, $C^6H^4(NO^2).CH^2Cl$, is formed by the action of chlorine at 150° – 200° , on orthonitrotoluene, as a viscid oil, having a pleasant aromatic odour, producing a burning sensation on sensitive parts of the skin, and solidifying after some time to a network of slender needles. It reacts with silver acetate, forming orthonitrobenzyl acetate, $C^6H^4(NO^2).CH^2(OC^2H^3O)$.

Orthonitrobenzyl Bromide is very much like the chloride, may be prepared in a similar manner, and produces an analogous reaction with silver acetate.

Para-nitrotoluene appears to react with halogens in the same manner as the ortho-compound (Wachendorff, *Ber.* viii. 1101).

Orthonitrochlorobenzene, $C^6NO^2.Cl.H^4$, is formed by the action of nitrous acid on paranitro-metachloraniline, $C^6.NO^2.Cl.H.NH^2.H^2$. It is solid at ordinary temperatures, melts at 32.5° , and boils at 243° . Jungfleisch's β -nitrochlorobenzene, described as liquid at ordinary temperatures (vii. 144), was probably impure (Beilstein a. Kurbatow, *Ber.* ix. 633).

Orthonitro-metadichlorobenzene, (1 : 2 : 4), or $C^6.NO^2.Cl.H.Cl.H^2$ (p. 186), yields by reduction with tin and hydrochloric acid, a chlorophenylenediamine from which the chlorine cannot be removed by sodium-amalgam (Beilstein a. Kurbatow, *Ber.* ix. 633). See, on the contrary, Körner (p. 186 of this volume). The same nitrodichlorobenzene heated with alcoholic potash yields a compound melting at 62° – 63° , probably $C^6H^3Cl(NO^2)(OC^2H^3)$ (B. and K.) *Nitro-orthodichlorobenzene*, $C^6.NO^2.H.Cl.Cl.H^2$ (p. 187), melting at 43° , is converted by heating with ammonia into a chloronitraniline, $C^6H^3Cl(NO^2)(NH^2)$, which crystallises in light yellow needles melting at 104° – 105° , easily soluble in alcohol and carbon sulphide. Its *acetyl-derivative* crystallises in colourless needles melting at 139° , and is converted by nitrous ether into metachloronitrobenzene (B. and K.)

Orthonitrometachloraniline, $C^6.NO^2.NH^2.H.Cl.H^2$ (m. p. 124° – 125°), is converted by heating with alcoholic soda into ethylic chloronitrophenate, $C^6H^3Cl(NO^2).OC^2H^3$ (Beilstein a. Kurbatow, *Liebig's Annalen*, clxxxii. 110).

Orthonitro-pararesol. See PHENOL, HOMOLOGUES OF.

Ortho-oxyphenylurethane. See OXYPHENYLURETHANE.

OSMIUM. Atomic Weight 200 (Deville a. Debray, *Compt. rend.* lxxxiii. 709). Crystallised osmium may be obtained by passing vapour of osmium tetroxide carried forward by a stream of nitrogen through a red-hot porcelain tube lined with pure carbon.* The osmium is thereby reduced, with formation of carbon dioxide, and the inner surface of the carbon cylinder soon becomes coated with metallic osmium, which prevents the carbon from acting directly on the osmium tetroxide. Part of the carbon, however, penetrates the layer of osmium and is oxidised to carbon monoxide, which meets the osmium tetroxide at a farther part of the tube and reduces it to metal. In this manner there is formed a tube of osmium very much like the tube of zinc oxide which is produced when zinc vapours issue and burn from a round opening. Frequently also this process is attended with the formation of copper-red crystalline scales, consisting of osmium sesquioxide, Os^2O^3 . Amorphous pulverulent osmium is readily produced by passing the vapour of osmium tetroxide mixed with carbon monoxide containing carbon dioxide through an ignited porcelain tube. This amorphous metal may be converted into crystallised osmium by fusing it in a graphite crucible with three or four times its weight of pure tin, dissolving out the excess of tin with hydrochloric acid, and finally heating the residual crystals in a stream of hydrochloric acid gas.

Pure osmium has a fine blue colour, with a grey to violet glitter; crystallises in thin funnel-shaped groups composed of cubes or of rhombohedrons very near to cubes; it is harder than glass, which it scratches, and has the highest sp. gr. of all known bodies, viz. 22.477 (uncor.)

Oxysulphides.—When an aqueous solution of osmium tetroxide is treated with hydrogen sulphide, a precipitate is formed which, when suspended in water, and submitted to the further action of hydrogen sulphide, yields a loosely crystalline body, easily oxidised on exposure to the air, and having the composition $Os^3S^7O^3.2H^2O$. The oxidation of this body by air at 70° – 80° yields an unstable, odourless, insoluble substance having the composition $OsSO^3.3H^2O$, and converted by further exposure to air into osmium tetroxide. The replacement of an atom of oxygen in osmium tetroxide by sulphur is attended with a complete alteration in the properties of the compound, osmium tetroxide being a stable strong-smelling substance soluble in water, whereas

* Such a lining may be formed by passing benzene-vapour through the red-hot tube.

the oxysulphide, OsSO_3 , is easily decomposable and peculiarly easy to reduce with hydrogen. Ammonia converts this oxysulphide, with separation of water and great rise of temperature, into a brown product, which contains osmium and nitrogen, in the atomic ratio 1 : 1, and gives off ammonia only after prolonged boiling with caustic soda (E. v. Meyer, *J. pr. Chem.* [2], xvi. 77).

On the separation of Osmium from Platinum, see PLATINUM.

OSSEIN. See PROTEIDS (Appendix to).

OSTEOLITE. According to Petersen (*Jahrb. f. Min.* 1873, 386), osteolite from the Rossberg, near Darmstadt, contains 34.7 per cent. phosphoric acid.

OSTRUTHIN. A neutral body obtained by Gorup-Besanez (*Ber.* vii. 564) from the root of Master-wort (*Imperatoria Ostruthium*) in treating that root with hot alcohol, with the view of obtaining pencedanin (iv. 386). The chopped roots were exhausted with hot alcohol; the filtrate freed from alcohol by distillation; the sticky residue exhausted with ether, with addition of a little petroleum-spirit (ligroïn); and the ethereal solution mixed with a quantity of ligroïn sufficient to produce a strong turbidity, and filtered after a resinous mass had separated from it. The filtrate freed from ether by evaporation yielded ostruthin in yellow rhombic crystals; and on leaving these to drain, dissolving them in potash, precipitating with carbonic acid, redissolving in alcohol, and precipitating with water, the ostruthin was obtained in slender, colourless silky needles whose composition is represented by the empirical formula $\text{C}^{14}\text{H}^{17}\text{O}^2$.

Ostruthin prepared as above is accompanied by a small quantity of another body containing less carbon and more hydrogen.

The following table exhibits a comparative view of the characters of imperatorin, pencedanin, and ostruthin:

Imperatorin of Osann and Wickenroder	Pencedanin of Schlatter, Bothe, and Erdmann	Ostruthin
Thick, well-formed, hard rhombic prisms or silky scales.	White, light prisms united into clusters.	Fine, white, silky needles.
Burning taste.	Burning acid taste.	Tasteless.
Melts at 75° .	Melts at 60° .	Melts at 115° .
Hardly soluble in cold spirits of wine.	Hardly soluble in cold spirit. The solutions yellow.	Easily soluble in cold spirit. The solutions fluorescent and colourless.
Soluble in ether.	Soluble in ether and petroleum spirit.	Soluble in ether; slightly soluble in petroleum spirit.
Insoluble in ammonia; slightly soluble in weak potash.	Soluble in hot ammonia and weak potash.	Soluble in cold ammonia and diluted potash.

From this comparison, Gorup-Besanez concludes that imperatorin and pencedanin are not identical, but distinct constituents of the root, produced at different stages of development of the plant. R. Wagner, on the other hand (*Ber.* vii. 590), regards them as identical.

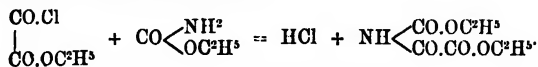
Ostruthin Hydrochloride, $\text{C}^{14}\text{H}^{17}\text{O}^2.\text{HCl}$, and the **hydrobromide**, $\text{C}^{14}\text{H}^{17}\text{O}^2.\text{HBr}$, are produced by passing gaseous hydrogen chloride and bromide into an alcoholic solution of ostruthin. The hydriodide has not been obtained.

Ostruthin fused with potash yields resorcinol, acetic acid, and butyric acid. Heated with *strong nitric acid*, it is violently attacked, with formation of oxalic acid; by prolonged boiling with *dilute nitric acid*, on the other hand, it yields styphnic acid.

With *bromine*, ostruthin yields substitution-products, viz. $\text{C}^{14}\text{H}^{15}\text{Br}^2\text{O}^2$ and $\text{C}^{14}\text{H}^{13}\text{Br}^4\text{O}^2$; with *chlorine*, mixtures for which no definite formulæ can be established. Heated with acetyl chloride it yields acetylostruthin in nacreous laminæ (Gorup-Besanez, *Liebig's Annalen*, clxxxiii. 321).

OXALAN. Syn. with OXALURAMIDE.

OXALCARBAMATE, ETHYLIC, $C^2H^{11}NO^3 = NH \begin{smallmatrix} \text{CO.OC}^2H^5 \\ \text{CO.CO.OC}^2H^5 \end{smallmatrix}$. This compound is formed by treating oxalic ethochloride with urethane in a flask with upright condenser, heated on an oil bath :



It crystallises from ether in tufts of vitreous brittle needles, dissolves in water, alcohol, and ether, but crystallises well only from the last. Melts at 45° (F. Salomon, *J. pr. Chem.* [2], ix. 290).

By heating oxamethane, $NH^2.C^2O^2.OC^2H^5$, with oxalic ethochloride, Salomon and Peitzsch obtained the compound $NH \begin{smallmatrix} C^2O^2.OC^2H^5 \\ C^2O^2.OC^2H^5 \end{smallmatrix}$, which they regard as isomeric with ethylic mesoxalcarbamate, $NH \begin{smallmatrix} \text{CO.OC}^2H^5 \\ C^2O^2.OC^2H^5 \end{smallmatrix}$. It crystallises from ether in radiate tufts of slender needles, melts at 67° , and decomposes with great facility. With alcoholic ammonia it yields oxamide; potassium ethylate added to its alcoholic solution immediately throws down potassium ethoxalate; silver oxide added to its aqueous solution throws down silver ethoxalate.

OXALETHYLINES. Wallach, by acting on diethyloxamide with phosphorus pentachloride, obtained a base, $C^6H^{10}ClN^2$, which he called chloroxalethylene (p. 453); and from this a number of other bases have been obtained by Wallach and Oppenheim (*Ber.* x. 1193).

Dioxalethylene, $C^{12}H^{18}N^4$, produced by the action of sodium on chloroxalethylene dissolved in petroleum-ether, boils above 300° , and forms an amorphous very sparingly soluble platinumchloride, $C^{12}H^{18}O^4.2HCl.PtCl^4$.

When chloroxalethylene dissolved in carbon disulphide is treated with bromine, two compounds are formed, chlorbromoxalethylene dibromide, $C^6H^8ClBrN^2.Br^2$, and a compound of this with hydrobromic acid, $C^6H^8ClBrN^2.Br^2.BrH$, which latter is also produced by the action of hydrobromic acid on the former dissolved in chloroform. The tetrabromine-compound is the less soluble of the two in chloroform. The tribromine-compound dissolves easily in chloroform, and separates in large red crystals melting at 133° . From measurements by Bodewig, these crystals appear to be monoclinic; $a : b : c = 2.0645 : 1 : 1.796$; angle $\beta = 74^\circ 27'$. Observed forms ∞P , $0P$, $-P \infty$, also $\infty P \infty$ and $\pm P$. Angle $\infty P : \infty P = 126^\circ 37'$; $\infty P : 0P = 96^\circ 55'$; $-P \infty : \infty P = 110^\circ 3'$. Both these bromine-compounds dissolve readily in carbon sulphide and in alcohol, their dissolution in the latter and in water being attended with separation of bromine. Alkaline solutions dissolve them slowly.

Bromchloroxalethylene Hydrobromide, $C^6H^8ClBrN^2.HBr$, is formed by boiling either of the bromine-compounds just described with water. The base separated therefrom is a thick, gradually solidifying oil. Its hydrochloride crystallises in hydrated prisms; the nitrate in curve-faced needles; the platinumchloride, $(C^6H^8ClBrN^2.HCl)^2PtCl^4$, in laminae. The argentonitrate, $(C^6H^8ClBrN^2)^2NO^3Ag$, dissolves easily in alcohol, sparingly in water, and crystallises from dilute alcohol in well-defined limpid prisms having a vitreous lustre. With other metallic salts this base forms precipitates similar to those obtained with chloroxalethylene. Bromchloroxalethylene is but slowly attacked by potash either in aqueous or alcoholic solution, but is completely decomposed by distillation; its hydrobromide is converted by hydrobromic acid into the tetrabromine-compound, $C^6H^8ClBrN^2.Br^2.BrH$.

The formation of the two bromine-compounds above described is often attended with that of a third, probably $C^6H^8ClN^2.Br^2$.

Iodine acts on chloroxalethylene in the same manner as bromine.

Chloroxethylene, the yield of which is usually 75 per cent. of the theoretical amount, is difficult to separate from diethyloxamide, and when contaminated therewith solidifies with comparative facility and completeness, whereas the perfectly pure base solidifies but very slowly, and only at very low temperatures.

OXALIC ACID, $C^2H^2O^4 = COOH.COOH$. On the occurrence of this acid in Fungi, see p. 832.

Formation.—Oxalic acid is produced, together with oxamic, carbamic, and carbonic acids, by oxidising ammonium glycinate, $C^2H^4(NH^4)NO^2$, with permanganate (Drechsel, *J. pr. Chem.* [2], xii. 417).

Preparation.—Experiments on the preparation of oxalic acid from sawdust and other vegetable matters have been made by W. Thorn (*Dingl. pol. J.* cxx. 24). A

weighed amount of sawdust was added to an alkaline solution of 30° – 42° Bm., which was kept boiling in an iron dish; strong solutions are to be preferred for this operation, as they prevent spitting of the melt. The results showed in the first place that the largest yield of oxalic acid is obtained by the use of pure potassium hydrate; a mixture of the hydrates of potassium and sodium yielded a smaller amount, and sodium hydrate alone a still smaller quantity. The highest yield obtained with soda alone was 52.14 per cent. of the sawdust used, 25 grams of sawdust being heated to 240° C with 100 grams NaHO in a thin layer. With a mixture of the two alkalis the yield was greater the larger the proportion of potash used, and with potash alone the yield was 65 per cent. of the wood employed. When however the wood was allowed to come more directly in contact with the air by being heated in a thin layer, different results were obtained. When 50 grams of wood were heated for 1–1½ hours with 100 grams of the alkaline hydrate of 40° Baumé in a layer 1 centimeter thick to 240° – 250° , pure sodium hydrate gave 33.14 per cent. of oxalic acid; 40 grams of potassium hydrate to 60 of sodium hydrate gave 80.57 per cent., and this did not differ materially from that obtained with pure potassium hydrate (81.23). When heated air was passed over the surface of the sawdust and alkali, the results obtained were not higher than the former. The addition of manganese dioxide had no influence on the reaction, the temperature being much too low to effect its decomposition.

Different sorts of wood yielded different amounts of oxalic acid.

	Per cent. of hygroscopic water	Per cent. oxalic acid	Per cent. oxalic acid calculated to wood dried at 100°
Pine	15.0	80.5	94.7
Poplar	14.0	80.1	93.14
Box	8.6	79.00	86.43
Oak	6.5	78.12	93.42

In the foregoing experiments 50 grams of wood were heated with 100 grams of alkali. When equal quantities of wood and alkali were employed, the yield of oxalic acid was larger in proportion to the quantity of alkali employed, and smaller in proportion to the wood. Thus, when heated in a thin layer, 50 grams of wood yielded oxalic acid equivalent to 81.0 per cent. of the wood employed, and to 40.0 per cent. of the alkali, and 100 grams of wood gave a quantity of oxalic acid equivalent to 54.14 per cent. of the wood and to 54.14 per cent. of the alkali.

To separate the oxalic acid from the melt, the latter is boiled with water, the solution concentrated to 38° Bm. (sp. gr. 1.35) and left to cool, whereupon nearly the whole of the oxalic acid separates in granules of sodium oxalate. This salt after washing is boiled with milk of lime; the resulting calcium salt is decomposed by sulphuric acid; and the liquid concentrated to 15 Bm. (sp. gr. 1.16), whereupon the dissolved gypsum crystallises out, and the solution freed therefrom and evaporated down to 30° Bm. (sp. gr. 1.261), yields crystals of oxalic acid.

The alkali contained in the several mother-liquors of this process may be recovered by concentration to sp. gr. 1.380, addition of sawdust till it assumes a pasty consistence, evaporation to dryness, and ignition. The mass is then treated with water or with the dilute alkaline liquor obtained after addition of milk of lime to the sodium oxalate, made caustic with lime, and after concentration till its specific gravity is 1.407, again heated with sawdust as at first.

C. O. Cech (*Dingl. pol. J.* cxxiv. 70) recommends as a substitute for sawdust, in the preparation of oxalic acid, the clippings of parchment paper, which can be obtained at a very cheap rate.

Purification.—To obtain pure oxalic acid for titration, E. Reichardt (*Arch. Pharm.* [3], ii. 235) stirs a hot saturated solution of the commercial acid till it is cold, and dries the fine-grained crystalline powder thus obtained between filter paper. Similar methods are recommended by L. Siebold (*Pharm. J. Trans.* [3], vi. 441), and F. Stolba (*Zeitschr. anal. Chem.* 1874, 50).

Estimation.—For the titration of oxalic acid and its salts, Jean a. Pellet (*Bull. Soc. Chim.* [2], xxvii. 204) recommend the use of baryta-water. The free acid is first exactly neutralised with soda, the solution then mixed with excess of baryta-water, and the uncombined baryta titrated back with sulphuric acid.

Reactions.—1. With Chlorates, Bromates, and Iodates. A boiling super-saturated aqueous solution of oxalic acid decomposes solutions of chlorates, bromates, and iodates, with evolution of chlorine, bromine, and iodine respectively. In the case of *potassium chlorate*, a large quantity of chlorine is evolved, but still a considerable quantity of the chlorate is reduced to chloride. With *potassium bromate* a similar reaction takes place, but the proportion of the bromine evolved to the bromide formed

is greater than that of chlorine to chloride in the case of the chlorate. *Iodates* evolve all their iodine in the free state, no traces of iodides being formed.

In the case of mixtures of these bodies, the chlorates are first decomposed, then the bromates, and finally the iodates, that which is attacked first being completely decomposed before the others are acted on. The steam accompanying the gas evolved expels all traces of it before vapours of the second halogen make their appearance. This can be distinctly seen, as there is a certain interval between the two reactions, it being necessary in some cases to add more oxalic acid to start it again.

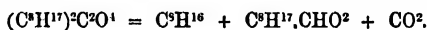
These reactions afford a means of testing chlorine and iodine in commercial bromine, also the purity of bromides and bromates. The bromine is dissolved in a slight excess of concentrated potash, and treated with oxalic acid. Bromides are oxidised to bromates by means of chlorine, and then treated with oxalic acid, and bromates are treated directly with oxalic acid (A. Guyard, *Bull. Soc. Chim.* [2], xxxi. 299).

2. With Potassium Permanganate. On the effect of temperature on the rate of action between this salt and oxalic acid, see CHEMICAL ACTION (p. 426).

3. With Sodium Silicate. When a solution of oxalic acid, 75 grams to the litre, is introduced into a vessel containing 500 c.c. of a solution of sodium silicate, the liquids do not mix, but a crust is formed at their surface of contact, consisting of amorphous hydrated silica. This crust sets quite hard, and decrepitates when heated, giving a fine white sand hard enough to polish glass (Monier, *Compt. rend.* lxxxv. 1053).

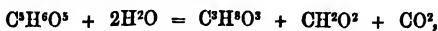
4. With Monatomic Alcohols. When a primary monatomic alcohol is treated with dehydrated oxalic acid, a large quantity of the corresponding oxalic ether is formed, whereas in the case of secondary alcohols, only a small quantity of an oxalic ether is obtained; thus 3 mols. *methyl alcohol* and 1 mol. oxalic acid heated together at 50° for several hours and then distilled, yielded carbon monoxide and dioxide, unchanged methyl alcohol, methyl oxalate about equal in weight to the oxalic acid employed, and a small quantity of methyl formate; *ethyl*, *normal propyl*, *isobutyl*, *isopentyl* (amyl), and *allyl alcohols* yield mixtures of normal and acid oxalic ethers. On subjecting the product to distillation, the normal ether goes over undecomposed, while the acid ether is resolved into carbon dioxide (with a little monoxide) and the corresponding formic ether, the quantity of the latter increasing with the proportion of oxalic acid, and in the case of ethyl alcohol, attaining the proportion of 0.28 formic to 1 pt. oxalic ether. *Benzyl alcohol* yielded only normal benzyl oxalate. *Pseudopropyl alcohol* reacts in general like the normal alcohol, but is less easily etherified.

Primary octyl alcohol from the essential oil of *Heracleum sphondylium*, on treatment with dehydrated oxalic acid yielded octylene (b.-p. 120°–125°), and octyl formate (b.-p. 195°–197°), these substances being formed by the decomposition of the octyl oxalate—



Secondary octyl alcohol (methyl-hexyl carbinol) under similar conditions gave carbon monoxide and dioxide, formic acid, and a small quantity of octyl formate. *Trimethyl carbinol* and *dimethyl-ethyl carbinol* are split up by the action of oxalic acid into water and hydrocarbons, viz., butylene and amylene respectively (Cahours a. Demarcay, *Compt. rend.* lxxxiii. 668; lxxxvi. 991).

5. With Polyatomic Alcohols (Lorin, 1873, *Ann. Chim. Phys.* xxix. 367; xxx. 447; *Compt. rend.* lxxvii. 129, 363; lxxxiv. 1136). It has long been known that oxalic acid when heated with glycerol (glycerin) and water is resolved into carbon dioxide and formic acid, ($\text{C}^2\text{H}^2\text{O}^4 = \text{CO}^2 + \text{CH}^2\text{O}^2$), the glycerol being commonly supposed to take no part in the reaction, but merely to prevent the temperature from rising so high as to give rise to the resolution of the formic acid into CO and H²O. It is remarkable, however, that the greater portion of the formic acid does not at once distil over, but remains in the retort together with the glycerol, and can be separated therefrom only by distillation with a considerable quantity of water (ii. 686). According to Lorin, the decomposition of oxalic acid under these circumstances into CO² and CH²O² is preceded by the formation of a glyceryl oxalate or oxalin, $\text{C}^3\text{H}^4\text{O}^5 = \text{C}^3\text{H}^4(\text{OH})(\text{O.CO})^2$, which when heated with water is resolved into glycerol, formic acid, and carbon dioxide; *



and in fact when a mixture of glycerol and oxalic acid is heated for some time at 65°

* When the mixture of glycerol and oxalic acid is heated without addition of water, the products are allyl alcohol, water, and carbon dioxide, $\text{C}^3\text{H}^4\text{O}^5 + \text{C}^2\text{H}^2\text{O}^4 = \text{C}^3\text{H}^5\text{O}^3 + 2\text{CO}^2 + 2\text{H}^2\text{O}$ (Tollens a. Henniger, vi. 80).

a product is obtained from which ether extracts a white silky body of unctuous aspect, easily altered by moisture, fusing readily in the dry state, and resolidifying at 53°. At a higher temperature it is said to be resolved into carbon monoxide and glycerol, and by distillation in a vacuum partly into aqueous formic acid and a gas. The aqueous solution of this body, which Lorin regards as a mixture, gave with ammonia a large quantity of oxanide, which compound was likewise obtained when mixtures of glycerol and oxalic acid in various proportions were heated at various temperatures, or left to themselves for some time; in the latter case the reaction takes place with peculiar facility when the anhydrous compounds are employed, and then treated with ammonia.

In the same manner are formed the oxalins of ethylene and octylene glycol, mannitol, dulcitol, erythritol, and quercitol, the temperature at which the decomposition of the oxalic acid begins being lower for the glycols, and higher for erythritol, &c., than for glycerol, with which it begins at 75°, and is in full activity at 90°; it is higher also for dulcitol than for mannitol. No action upon oxalic acid is exerted by cane-sugar, grape-sugar, milk-sugar, or orcinol; hydrate of turpentine-oil heated with oxalic acid is resolved into turpentine-oil and water. Monatomic alcohols heated with oxalic acid exhibit only a faint turbidity. Lorin regards the reaction with oxalic acid above described as characteristic of polyatomic alcohols.

Metallic Oxalates. On the Heat of Formation and Solution of Oxalates, see HEAT, pp. 954, 957, 958, 982.

On the Action of Alkaline Oxalates on Earthy Carbonates, and of Alkaline Carbonates on Earthy Oxalates, see CARBONATES (p. 410).

Electrolysis.—According to Bungo (*Ber.* ix. 78), aqueous solutions of oxalates yield by electrolysis hydrogen at the negative pole, and at the positive, either carbon dioxide alone or a mixture of that gas with oxygen. The proportion of these two gases in the mixture varies according to the conditions of the experiment, the relative quantity of oxygen being increased by strengthening the current, enlarging the surface of the anode, using stronger solutions, and lowering the temperature.

Ammonium Oxalate, $C^2(NH^4)^2O^4$.—This salt has been found, to the amount of 5.54 per cent., in Guanapi guano, in combination with 2 mols. water, the ordinary salt containing 1 mol. (J. A. Tanner, *Chem. News*, xxxii. 162).

Calcium Oxalate may be obtained in crystals of the various forms occurring in plants, and others besides, by causing solutions of potassium oxalate and calcium chloride, or of oxalic acid and calcium sulphate, to mix slowly in a liquid medium by means of strips of filter-paper or dialysing diaphragms, the particular forms obtained varying according to the nature of the reaction and the constitution of the medium. Thus in a medium containing glucose or dextrin, needles are formed exactly like the 'raphides' occurring in plants; in a medium containing a small quantity of albumin, crystals of hour-glass shape are produced, like those which sometimes occur in urine (Vesque, *Compt. rend.* lxxviii. 149). Similar results were previously obtained by Monnier (vi. 887).

Potassio-calcio-chromic Oxalate, $KCaCr(C^2O^4)^3$, is formed by mixing warm dilute solutions of blue potassio-chromic oxalate and calcium chloride: $K^3Cr(C^2O^4)^3 + CaCl^2 = 2KCl + KCaCr(C^2O^4)^3$; or by boiling a solution of red potassio-chromic oxalate with recently precipitated calcium oxalate: $KCr(C^2O^4)^2 + CaC^2O^4 = KCaCr(C^2O^4)^3$. The former method is to be preferred.

This salt loses 1 mol. of water in a dry atmosphere, changing from a greenish-black to a greenish-violet tint; at 100° it is dehydrated and becomes violet. 1 pt. of it dissolves in about 22 of water at 16°, and in 5 pts. at 100°. The solution, of a greenish-purple colour, becomes more decidedly green when boiled, and resumes its original colour on cooling. The salt is exceedingly stable, and crystallises with the greatest ease from hot or cold, acid or neutral solutions, and can be precipitated in the crystalline state. It is almost insoluble in strong hydrochloric acid. The crystals, when slowly deposited, are formed in clusters, the individual crystals being never more than $\frac{1}{400}$ of an inch in thickness and $\frac{1}{2}$ an inch long. They have a greenish-black lustre, and apparently consist of prisms with a rectangular base; they reflect white light. From hot solutions much smaller crystals are deposited, which, as well as their powder, are olive-green in daylight, and beetroot-red by gaslight. Minute crystals, examined in daylight by the microscope, are of a pale green tint; fragments of large crystals coarsely powdered appear of almost all tints, rich-green and blue prevailing. Larger crystals, deposited by spontaneous evaporation of a cold solution, appear of two colours, chiefly a beautiful blue and rich green, with sometimes a tinge of deep red.

A crystal mounted in such a manner that it could be rotated on its principal crystalline axis while under microscopic examination, showed in each revolution two phases of blue, two of green, and two of opacity with a tinge of red. When a crystal so small as to be quite transparent in any position was examined in this manner, pure red light was transmitted through its edges. These effects show that the play of colour is due to pleochroism, or the property which, by virtue of double refraction, some minerals possess of transmitting light of different tints through their different crystalline axes. The two axes of *thin* crystals give spectra which do not differ from each other materially, or from the solution of this salt in particular, or from chromium salts generally.

By examination with a Nicol's prism, and with similar crystals used as analysers, it was found that this salt is a powerful polariser. There is a marked difference when the blue and the green rays are examined with a Nicol's prism, the former being much more completely polarised than the latter, so that in rotating the Nicol there is an alternation of brilliant blue and perfect darkness, or, if the crystal be thin, of blue and reddish-green. If, however, a crystal transmitting green rays of equal brilliancy be examined, the light is not cut off, but only obscured. In like manner, if both analyser and polariser consist of these crystals, the effect when they are in a position at right angles to each other is the same as that produced by a Nicol's prism, viz., only green rays are transmitted. The green ray is more strongly refracted, and at the same time more absorbed than the blue, in accordance with Babinet's law (*Pogg. Ann.* xli. 116). This was made evident from the apparent change of colour when white light was admitted to them at different angles. These observations account for the facts already noticed—namely, that minute crystals appear green even under the microscope, and also that the powder is green.

Taking a number of crystals, or fragments of crystals, lying in all directions over each other, it is easy to see that no blue rays can be transmitted; for where two crystals cross, the light transmitted is green. The green rays being more absorbed (that is to say, travelling with less facility) than the blue, it is possible to have a blue crystal so thin as to transmit white light through one axis, while green rays would pass at right angles through the other; under these circumstances the crystals would appear green. The red colour seen by gaslight is of course due to the suppression of the green and blue by the yellow illumination. This substance strikingly exemplifies the fact that pleochroism results from the polarisation of light traversing a doubly-refracting coloured medium.

This chromium-compound is a remarkably delicate test for the purity of white light, showing a red tint by gas-light, red and blue by the lime-light, while by the light of magnesium wire or the sun it displays red, blue, and green. Altogether it is the most remarkable example of pleochroism at present known (W. N. Hartley, *Proc. Roy. Soc.* xxi. 499).

From the microscopic examination of many similar compounds, it was found that the efficiency in displaying pleochroism is inversely as the molecular weight of the compounds, the property depending upon the amount of colour the chromium gives to the crystals.

Monorubidium Dioxalate, $\text{RbHC}^2\text{O}^4 \cdot \text{C}^2\text{H}^2\text{O}^4 + 2\text{H}^2\text{O}$, is prepared by digesting together 100 grams of rubidium-alum, 72.6 grams of crystallised oxalic acid, and 170 c.c. water at the boiling heat, and separates out almost completely on cooling. By slow evaporation it is obtained in fine, transparent, many-faced prismatic crystals, apparently triclinic; and by cooling from a hot concentrated solution, in translucent laminar groups of crystals, becoming milk-white when dried at 100° , but not efflorescing perceptibly in the air. The pulverised salt has a density of nearly 2.1246 at 18° . The salt dissolves very easily in boiling water, and in 47 pts. water at 21° , the latter solution having a density of 1.0111. By ignition it is converted into carbonate (Stolba, *Münch. Akad. Ber.* 1877, 6 Heft).

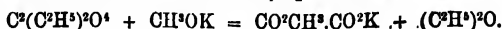
Vanadious Oxalate is obtained, according to Guyard (*Bull. Soc. Chim.* [2], xxv. 350), by fusing a mixture of vanadium pentoxide and crystallised oxalic acid in the water of crystallisation of the latter. The blue mass thus obtained dissolves completely in water, forming a solution which on evaporation yields crystals of the oxalate.

Oxalic Ethers. On the reaction of Ethyl and Methyl Oxalates with Naphthylamine, see NAPHTHYLAMINE.

Methyl Oxalate, $\text{C}^2(\text{CH}^3)^2\text{O}^4$, is very easily prepared by dissolving oxalic acid dehydrated at 100° in boiling methyl alcohol, and leaving the solution to cool. The crystals are freed from adhering mother-liquor by draining on a vacuum-filter, and washed with cold water till the liquid which runs away no longer exhibits the iodoform

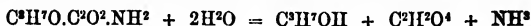
reaction. To obtain pure methyl alcohol from this ether, it must be decomposed by prolonged boiling with water and distilled (Erlenmeyer, *N. Rep. Pharm.* xxiii. 624).

Ethyl Oxalate, $C^2(C^2H^5)^2O^4$.—With *potassium methylate*, this ether forms potassium methyloxalate (Salomon, *Ber.* viii. 1506); possibly thus:



On the reaction of Ethyl Oxalate with Cyanamide, see p. 598.

Propyl Oxalate, $C^2(C^3H^7)^2O^4$, is obtained by distilling anhydrous propyl alcohol with dehydrated oxalic acid, either alone or mixed with one-third of its weight of sulphuric acid. The distillate, on addition of water, separates into two layers, the upper of which, when dried and rectified, yields propyl oxalate, having an aromatic odour, a density of 1.018 at 22°, and boiling between 209° and 211°. Ammonia easily converts it into crystalline propyl oxamate, $C^3H^7.O.CO.CO.NH^2$, which is decomposed by water with reproduction of propyl alcohol and oxalic acid:



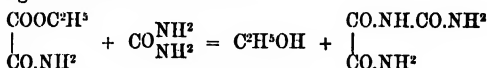
(Cahours, *Compt. rend.* lxxvii. 749).

Butyl Oxalate, $C^2(C^4H^9)^2O^4$, obtained in like manner, is a very clear, colourless liquid, having a strong aromatic odour, and a density of 1.002 at 14°. It mixes in all proportions with alcohol and ether, but is insoluble in water. Cold water decomposes it slowly; boiling potash-ley more quickly, into oxalic acid and butyl alcohol. By treatment with an alcoholic solution of *potassium hydroxide* containing only a quantity of potassium sufficient to replace one of the butyl-molecules, it is converted into potassium-butyl oxalate, $CO^2C^4H^9.CO^2K$. With *aqueous ammonia* it forms oxamide. By addition of *alcoholic ammonia* in small portions it is converted into butyl oxamate, $NH^2.CO.CO.O.C^4H^9$, which separates from its solution on spontaneous evaporation in beautiful prisms (Cahours, *ibid.* 1408).

OXALIS. Experiments have been made by Mercalante (*Gazz. chim. ital.* 1875 249) on the growth of wood-sorrel (*Oxalis acetosella*) and several species of *Rumex* in sulphur, to which were added altogether 11 pts. per thousand of ferric oxide, and of the nitrates, phosphates, sulphates, and silicates of sodium, calcium, and magnesium, but no salts of potassium. Under these circumstances the plants did not fructify; their juice contained only an eighth of the quantity of acid present in that of the normal plants; tartaric acid was present as well as oxalic acid; and the proportion of starch and of sugar was greatly diminished.

OXALURAMIDE, $C^3H^3N^3O^3 = \begin{array}{c} CO.NH.CO.NH^2 \\ | \\ CO.NH^2 \end{array}$. *Oxalan*.—This compound is

formed by fusing oxamethane with urea:



(Carstanjen, *J. pr. Chem.* [2], ix. 143); also by heating ammonium parabanate, $C^3H(NH^2)^2N^2O^3$ (with which it is metameric) with alcoholic ammonia (anhydrous alcohol saturated at ordinary temperatures with NH^3) at 100° in a sealed tube for six or eight hours.

The *amide of dimethyloxaluric acid*, $\begin{array}{c} CO.N(CH^3).CO.NH(CH^3) \\ | \\ CO.NH^2 \end{array}$, is formed in like

manner by the action of an alcoholic solution of ammonia at ordinary temperatures on dimethylparabanic acid. It crystallises in needles melting at 223.5° (Menschutkin, *Ber.* vii. 128; *Liebig's Annalen*, clxxii. 73).

OXALURIC ACID, $C^3H^3N^2O^4 = NH^2.CO.NH.CO.COOH$ (Menschutkin, *ibid.* 89). The potassium salt of this acid, $C^3H^3KN^2O^4$, is formed by the action of water on potassium parabanate, $C^3HKN^2O^3$. According to Strecker (*ibid.* cxiii. 47), it is also produced by the action of potassium carbonate on alloxan in presence of hydrocyanic acid; Menschutkin, however, obtained by this process another salt, the composition of which has not been determined. *Potassium oxalurate* is sparingly soluble in water and crystallises with great facility. Even small quantities of it yield fine well-developed crystals, containing 1 mol. water, which is given off at 100°, and slowly by efflorescence in contact with the air. According to measurements by Erofejeff, they belong to the orthorhombic system. Axial ratio, $a : b : c = 1 : 0.6014965 : 0.5393226$. Observed forms, $P, \infty P, \bar{P} \infty, \infty \bar{P} \infty$.

By the action of *phosphorus oxychloride*, oxaluric acid is converted into *oxalyl*—

carbamide or parabanic acid: $C^3H^4N^2O^4 - H^2O = C^3H^2N^2O^3$ (Grimaux, *Compt. rend.* lxxvii. 1548).

Ethyl Oxalurate, $NH^2.CO.NH.C^2O^2.O^2C^2H^3$, which L. Henry obtained by the action of ethoxyoxalyl chloride, $C^2H^3O.C^2O^2.Cl$, on urea (vii. 883) may also be prepared by heating silver oxalurate for half an hour in a reflux apparatus with a slight excess of ethyl bromide or iodide dissolved in absolute alcohol. It melts with decomposition at $177^\circ-178^\circ$; is converted by silver nitrate into diargentic parabanate, $C^3Ag^2N^2O^3$, and resolved by baryta-water into oxalic acid, urea, and alcohol; by alcoholic ammonia, at 120° , into oxaluramide and alcohol; by hot water and dilute acids into oxalic acid, urea oxalate, and other products (F. Salomon, *Ber.* ix. 374).

OXALYL-CARBAMIDE. Syn. with PARABANIC ACID (*q. v.*)

OXALYL-DIPHENYL-HYDRAZIDE, $(C^6H^5.N^2H^3)^2C^2O^2$. See HYDRAZINES (p. 1053).

OXAMETHANE, $NH^2.CO.CO.O^2C^2H^3$. *Ethyl Oxamate*. See OXAMIC ETHERS.

OXAMIC ACID, $C^2H^2NO^3 = NH^2.CO.CO.OH$. This acid is formed by the direct oxidation of glycocine, $NH^2.CH^2.CO.OH$, with potassium permanganate. Oxalic and carbonic acids, which are formed at the same time, may be removed by calcium chloride, the oxamic acid then precipitated by solution of basic lead acetate, and the precipitate decomposed by hydrogen sulphide (R. Engel, *Compt. rend.* lxxix. 808).

OXAMIC ETHERS.

Ethyl Oxamate or Oxamethane, $C^4H^7NO^3 = NH^2.CO.CO.O^2C^2H^3$, is best prepared, according to Weddige (*J. pr. Chem.* [2], x. 193), by adding very gradually to a solution of 1 mol. ethyl oxalate in two or three times its volume of alcohol, 1 mol. ammonia likewise dissolved in alcohol, the whole being carefully cooled by ice, as rise of temperature would lead to the formation of considerable quantities of oxamide. The oxamethane separates, even while the process is going on, in thick crystals, which at the end of the reaction must be freed from small quantities of oxamide by recrystallisation from hot alcohol. The mother-liquor yields additional quantities on evaporation.

On the formation of Oxaluramide by fusing Oxamethane with Urea, see p. 1455.

By the action of *phosphorus pentachloride*, oxamethane is converted into ethylic dichloramidacetate, $NH^2.CCl^2.COOC^2H^3$, which crystallises in hard white needles; fumes in the neighbourhood of ammonia; is reconverted by water into oxamethane; gives off chlorine when kept for some time, and hydrogen chloride when fused, with simultaneous formation of ethylic cyanocarbonate. If the temperature rises somewhat too high during the preparation of the dichloramidacetate, a body is formed having the composition $NH=CCl-COOC^2H^3$ (Wallach, *Ber.* viii. 299).

In the distillation of oxamethane with phosphorus pentachloride, there are also formed, in consequence of the action of water, fine crystals melting at $128^\circ-130^\circ$, and having the composition $C^4H^6O^3Cl^2NP$. This compound dissolves slowly in cold water and in acids, easily in alkalis and ether. When heated above its melting point, it is resolved into phosphorus oxychloride and ethyl-cyanocarbonic acid. Water decomposes it, forming hydrochloric but no phosphoric acid, showing that it is not a compound of ethylcyanocarbonic acid with $POCl^3$, but that its constitution is probably $C^2H^3O.CO.CCl^2.NH.POCl^2$ (Wallach).

Oxamethane Cyanurate, $(C^4H^7NO^3)^3C^3H^3N^3O^3$, metamerie and polymeric with ethyl oxalurate, is obtained by passing the vapour of cyanic acid into 5 grams of pure and dry oxamethane heated to 130° in an oil-bath, treating the product with 30–40 grams of boiling water, and filtering. The cyanurate then separates in needles, which may be purified from oxamethane, if still present, by recrystallisation. It crystallises in shining brittle needles nearly insoluble in cold water, soluble in about 30 pts. of boiling water; melts to a pasty mass at $155^\circ-160^\circ$; and is resolved at a higher temperature into cyanic acid and a crystalline sublimate. On boiling it for a few minutes with milk of lime, and filtering, the filtrate deposits hard shining prisms of calcium oxamate. Ammonia added to its aqueous solution precipitates crystals of oxamide, and baryta-water throws down barium cyanurate. These reactions demonstrate the composition of the compound (Grimaux, *Bull. Soc. Chim.* [2], xxi. 153).

Acetyl-oxamethane, $NH(C^2H^3O).C^2O^2.C^2C^2H^3$, formed by heating oxamethane with acetyl chloride, crystallises in radiate groups of needles, soluble in alcohol and ether, melting at 54° . The compound thus formed is probably identical with that which Ossikovsky obtained (*Ber.* v. 667) by the action of ethoxyoxalyl chloride on acetamide (Kretschmar a. Salomon, *J. pr. Chem.* [2], ix. 299).

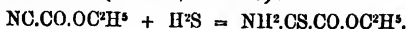
Benzoyl-oxamethane, produced in a similar manner, is also a finely crystallised compound.

Ethylloxamethane, $\text{NH}(\text{C}^2\text{H}_5)\cdot\text{C}^2\text{O}^2\cdot\text{OC}^2\text{H}_5$, formed by the action of ethyl oxalate on ethylamine, is an oily liquid boiling at 244° – 246° , miscible in all proportions with water, soluble in alcohol and in ether. It is completely decomposed by aqueous ammonia with formation of ethylloxamide, $\text{NH}(\text{C}^2\text{H}_5)\cdot\text{C}^2\text{O}^2\cdot\text{NH}^2$. It is saponified by boiling water, also by milk of lime, with great rise of temperature and formation of a crystalline ethylloxamate of calcium containing 2 mol. H^2O . The acid obtained from this salt sublimes in woolly needles (Wallach a. West, *Ber.* viii. 760).

Ethylloxamethane is converted by PCl_5 into *ethylloxamethane-amidochloride*, $\text{C}^2\text{H}_5\cdot\text{NH}\cdot\text{CCl}^2\text{—COOC}^2\text{H}_5$, which by prolonged heating at 100° is resolved into HCl , $\text{C}^2\text{H}_5\text{Cl}$, CO^2 , and greasy substances, from which a very small quantity of a body melting at 200° may be sublimed (Wallach a. West, *Ber.* viii. 760; ix. 262).

Methylloxamethane, $\text{NH}(\text{CH}^3)\cdot\text{C}^2\text{O}^2\cdot\text{OC}^2\text{H}_5$, obtained by passing methylamine into ethyl oxalate, solidifies at 0° , but at ordinary temperatures is an oil soluble in water (Wallach a. West).

Ethyl Thioxamate, $\text{NH}^2\cdot\text{CS}\cdot\text{CO}\cdot\text{OC}^2\text{H}_5$, is formed by addition of hydrogen sulphide to ethyl cyanocarbonate (vii. 415; viii. 617):



When hydrogen sulphide is passed into this ether or its alcoholic solution, ethyl thioxamate soon separates in yellow crystals, and after some time the entire liquid solidifies to a crystalline pulp; and by pressing out the mother-liquor and recrystallising from ether, the thioxamate is obtained in large lemon-yellow prisms; from hot water it crystallises in needles. It melts at 63° – 64° , and cannot be distilled without decomposition (Weddige, *J. pr. Chem.* [2], vii. 79).

Methyl Thioxamate, $\text{NH}^2\cdot\text{CS}\cdot\text{CO}\cdot\text{OCH}^3$, produced in like manner, crystallises in delicate light-yellow, brilliant needles or laminæ; melts at 86° ; dissolves in alcohol and ether, less easily in water; decomposes when heated above its melting point (*ibid.* x. 193).

Isobutyl Thioxamate, $\text{NH}^2\cdot\text{CS}\cdot\text{CO}\cdot\text{CH}^2\cdot\text{CH}(\text{CH}^3)^2$, crystallises from alcohol in long lemon-yellow needles and prisms, which melt at 58° , dissolve with moderate facility in alcohol and ether, sparingly in water (Weddige, *loc. cit.*)

Phenyloxamic Ethers (H. Klinger, *Ber.* viii. 310). *Ethyllic Phenyloxamate*, or *Phenyloxamethane*, $\text{C}^6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{COOC}^2\text{H}_5$, is formed by heating ethyl oxalate and aniline together in molecular proportions, and crystallises in large plates or prisms, melting at 66° , and dissolving readily in ether, alcohol, and benzene. From water it crystallises in small needles, melting at 64.5° – 65° . *Acetyl chloride* converts it into ethyl phenylacetyloxamate, $\text{C}^6\text{H}_5\cdot\text{CO}\cdot\text{N}(\text{C}^2\text{H}_5\text{O})\cdot\text{COOC}^2\text{H}_5$, which forms large prisms or plates melting at 66° – 67° . When the phenyloxamate is treated with bromine, the monobromophenyl-compound, $\text{C}^6\text{H}_4\text{Br}\cdot\text{CONH}\cdot\text{COOC}^2\text{H}_5$, is formed, crystallising in plates or flat needles which melt at 154° – 156° , and yield on saponification parabromaniline melting at 61° – 62° .

Ethyllic phenyloxamate heated, not above 70° , with phosphorus pentachloride is converted into ethylic phenylamidodichloracetate, $\text{NH}(\text{C}^6\text{H}_5)\cdot\text{CCl}^2\cdot\text{COOC}^2\text{H}_5$; above 70° , however, an imidochloride is produced. By heating the amidodichloracetate for a long time to 90° , or for a shorter time to 120° , or subjecting it to the action of gaseous ammonia, it is converted into ethylic phenylimidochloracetate, $\text{C}^6\text{H}_5\text{N}=\text{CCl}^2\text{—CO—OC}^2\text{H}_5$, which crystallises in colourless needles melting at 91° . Both the amidodichloracetate and the imidomonochloracetate are converted by aniline into the compound $\text{C}^6\text{H}_5\cdot\text{N}=\text{C} \begin{smallmatrix} \text{NH}\cdot\text{C}^6\text{H}_5 \\ \text{CO}\cdot\text{NH}\cdot\text{C}^6\text{H}_5 \end{smallmatrix}$ which crystallises in yellow-green laminæ, melts at 234° – 235° , and is resolved by boiling with water into oxanilide (m. p. 245°) and aniline. When the amidodichloracetate is heated for twelve hours at 90° , or for two or three hours at 120° – 130° , CO and CO^2 are given off, and the residual liquid is found to contain nothing but ethylic phenyloxamate and aniline.

Ethyllic Paratolyloxamate or **Paratolyloxamethane** $\text{C}^6\text{H}_4(\text{CH}^3)\cdot\text{CO}\cdot\text{NH}\cdot\text{COOC}^2\text{H}_5$, obtained by heating ethyl oxalate with paratoluidine, crystallises in laminæ and melts at 66° – 67° . Paratolyloxamic acid, obtained from it by the action of alkalis, forms needles melting at 168° – 170° . *Phosphorus pentachloride* converts paratolyloxamethane into ethylic paratolyamidodichloracetate, $\text{C}^6\text{H}_4(\text{CH}^3)\cdot\text{NH}\cdot\text{CCl}^2\cdot\text{COOC}^2\text{H}_5$, which crystallises in white needles melting at 59° – 60° , and is converted by water, or by alcohol of 98 per cent., into paratolyloxamethane (Klinger).

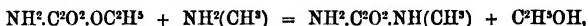
Phenylene (Meta-) Oxamic Acid, $\text{C}^6\text{H}^4\text{N}^2\text{O}^3 = \text{H}^2\text{N}\cdot\text{C}^6\text{H}^4\cdot\text{NH}\cdot\text{C}^2\text{O}^2\cdot\text{OH}$, is

produced, together with the corresponding phenylenediamine oxalate, when meta-phenylenediamine is boiled with oxalic acid and alcohol for five or six hours, and separates out, while the easily soluble phenylenediamine oxalate remains in the liquid. It likewise separates when a solution of phenylenediamine oxalate is boiled for a considerable time, and is obtained in greatest abundance when a solution of meta-phenylenediamine is gradually added to a boiling solution of oxalic acid. It crystallises from boiling water in slightly reddish needles, which melt only at a very high temperature and carbonise at the same time. The *ammonium salt* forms slightly yellow crystals, sparingly soluble in pure water, easily in slightly alkaline water. The *silver salt* forms long slender needles (Klusemann, *Ber.* vii. 1261).

OXAMIDE, $\text{NH}_2\cdot\text{C}^2\text{O}^2\cdot\text{NH}_2$. On the Heat of Formation of Oxamide, see p. 960.

Reaction with Alcohols.—Oxamide, like other amides, does not yield aminobases when heated with alcohols. Thus, on distilling it with sodium ethylate or with sodium or potassium phenate, not a trace of ethylamine or phenylamine is obtained, the only products being ammonia and cyanide of sodium or potassium. Considerable quantities of potassium cyanide are formed on heating oxamide with potassium hydrate (Weith, *Ber.* vi. 966).

Methyloxamide, $\text{NH}_2\cdot\text{C}^2\text{O}^2\cdot\text{NH}(\text{CH}_3)$, prepared by the action of methylamine on oxamethane:



crystallises in microscopic needles melting at $227^\circ\text{--}229^\circ$, sparingly soluble in water and in alcohol (Wallach a. West, *Ber.* ix. 262).

Methylethyloxamide, $\text{NH}(\text{CH}_3)\cdot\text{C}^2\text{O}^2\cdot\text{NH}(\text{C}^2\text{H}_5)$, obtained in like manner from methylamine and ethyloxamethane, crystallises from alcohol in needles melting at $155^\circ\text{--}157^\circ$, subliming easily, soluble in hot water. By the action of phosphorus pentachloride, it is converted into chloroxalmethylethylene, $\text{C}^3\text{H}^7\text{ClN}^2$, an oily liquid boiling at $212^\circ\text{--}213^\circ$, miscible with water, and solidifying at low temperatures. Its *hydrochloride*, $\text{C}^3\text{H}^7\text{ClN}^2\cdot\text{HCl}$, is very hygroscopic, but crystallises on standing over sulphuric acid; the *platinochloride*, $(\text{C}^3\text{H}^7\text{ClN}^2\cdot\text{HCl})^2\text{PtCl}_4$, crystallises from alcohol in large tablets; the *silver salt*, $\text{C}^3\text{H}^7\text{ClN}^2\cdot\text{NO}^2\text{Ag}$, crystallises in transparent prisms; the *methiodide*, $\text{C}^3\text{H}^7\text{ClN}^2\cdot\text{CH}_3\text{I}$, is very stable, and is purified by crystallisation from alcohol. The reaction of chloroxalmethylethylene with metallic salts closely resembles those of its homologues previously described (pp. 453, 454) (Wallach a. West).

Phenylmethyloxamide, $\text{NH}(\text{CH}_3)\cdot\text{C}^2\text{O}^2\cdot\text{NH}(\text{C}^6\text{H}_5)$, from methyloxamethane and aniline, crystallises in thin white needles, melting at $171^\circ\text{--}173^\circ$, easily sublimable.


Phenylethyloxamide, $\text{NH}(\text{C}^2\text{H}_5)\cdot\text{C}^2\text{O}^2\cdot\text{NH}(\text{C}^6\text{H}_5)$, prepared from ethyloxamethane and aniline, or from ethylic phenyloxamate and ethylamine, is very slightly soluble in water, but may be crystallised from alcohol in white shining needles of silky softness, and melting at 169° (Wallach a. West).

OXAMOYDIN. A compound formed by the action of cyanogen on albumin. See PROTEIDS.

OXETHYLENE-TOLUIDINE, $\text{C}^8\text{H}^{13}\text{NO} = \text{NH}(\text{C}^3\text{H}_7)(\text{C}^3\text{H}_4\text{OH})$. See TOLUIDINES.

OXIMIDOCYANIC ACID. Syn. with PARAHANIC ACID.

OXINDOLE, $\text{C}^8\text{H}^7\text{NO}$. The identity of this compound with orthoamidophenyl-
 CH_2CO

acetic anhydride, , has been already noticed (p. 1086); and this view of its constitution is confirmed by its formation by reduction of orthonitrophenylacetic acid. When a mixture of the three isomeric nitrophenylacetic acids is subjected to the action of tin and hydrochloric acid, and the product is neutralised with marble and precipitated with barium carbonate, the para- and meta-amido-acids form barium salts, while the ortho-acid remains dissolved in the form of an anhydride, which may be extracted by ether. This anhydride is identical with oxindole, prepared by reduction of dioxindole (vi. 736), and yields indole when heated with zinc-dust (A. Baeyer, *Ber.* xi. 582).

After the ingestion of oxindole and dioxindole (by men, dogs, and rabbits), red colouring matters are found in the urine, very much like those which are produced by the oxidation of these bodies in the air (Nencki, *Ber.* vii. 1593).

OXONIC ACID, $\text{C}^8\text{H}^8\text{N}^2\text{O}^4$. An acid discovered by Strecker, who obtained it by the action of atmospheric oxygen on uric acid in alkaline solution. It forms two

series of salts. The *acid potassium salt*, precipitated by acetic acid from the alkaline solution just mentioned, crystallises in needles with $1\frac{1}{2}$ mol. water. The *acid barium salt* contains $\frac{1}{2}$ mol. water. These salts were found by L. Medicus among the preparations left by Strecker (*Liebig's Annalen*, clxxv. 230).

OXYACETANILIDE, $C^6H^5NO^2 = C^6H^5.NH.C^2H^2(OH)O$. Syn. with PHENYL-HYDROXYL-ACETAMIDE. See ACETAMIDES (p. 7).

OXYACETOTOLUIDINE, $C^6H^{11}NO^2 = C^6H^4(CH^3).NH.C^2H^2(OH)O$ (*loc. cit.*)

OXYACRYLIC or **ACRYL-LACTIC ACID**,



The barium salt of this acid is formed, together with barium malonate (p. 1257), by the prolonged action of boiling baryta-water on ethyl chloracrylate (Pinner & Bischoff, *Liebig's Annalen*, clxxix. 85).

OXYANTHRAQUINONES. See ANTHRAQUINONES (pp. 99-112).

OXYAZOBENZENE, $C^{12}H^{10}N^2O = C^6H^5.N=N.O.C^6H^5$, is formed when a mixture of nitrosophenol (20 pts.) and aniline acetate (60 pts.) is left to itself at ordinary temperatures or heated on the water-bath. A brisk action takes place, attended with change of colour and formation of a crystalline pulp, which, when heated with ammonia, yields a solution of oxyazobenzene. This compound crystallises in orange-coloured prisms, melting at 148° (Kimich, *Ber.* viii. 1499); compare vii. 151; viii. 215.

OXYAZOTOLUENE, $C^6H^4(CH^3).N=N.O.C^6H^4(CH^3)$, formed, together with other products, by the action of paratoluidine acetate on nitrosophenol, crystallises in orange-red prisms melting at 151° , somewhat soluble in hot water. It possesses acid properties, and yields a silver salt crystallising in shining orange-coloured needles (Kimich, *loc. cit.*)

OXYBENZALDEHYDES. See OXYBENZOIC ALDEHYDES (p. 1865).

OXYBENZAMIDE (PARA-). See OXYBENZOIC ACIDS (p. 1463).

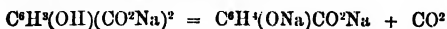
OXYBENZENE, or **OZOBENZENE**. An explosive substance formed by treating benzene with ozonised oxygen (p. 159).

OXYBENZOIC or **HYDROXYBENZOIC ACIDS**, $C^6H^4(OH).COOH$. Many of the reactions and derivatives of these acids have already been described (pp. 278-294). The following are recent additions to our knowledge of them, which have been made by H. Kupferberg (*J. pr. Chem.* [2], xvi. 424).

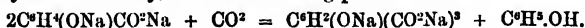
Normal Sodium Paraoxybenzoate, heated to 240° - 250° , is resolved into a basic salt, phenol, and carbon dioxide, according to the equation:



If the operation is conducted in a stream of carbon dioxide, and the temperature raised to 280° - 295° , the basic salt is left as a white residue, which is then found to yield 36 per cent. of salicylic acid, the quantity decreasing with the rise of temperature. The change of paraoxybenzoic acid into salicylic acid may perhaps be regarded as due to the action of carbon dioxide, and to a more complex action than the mere change of position of the hydroxyl and carboxyl groups, possibly to the formation of an isomeride of orthophenoldicarboxylic acid, which would be resolved by heat into basic sodium salicylate and carbon dioxide, as follows:



This view is supported by the following observations:—(1.) When sodium paraoxybenzoate is heated in a quick stream of hydrogen, no salicylic acid is formed; if the stream is slow, a small quantity is produced. (2.) By Van den Welden's observation (*J. pr. Chem.* [2], xv. 155), that thallous salicylate when heated decomposes into paraoxybenzoic and orthophenoldicarboxylic acids. (3.) By Ost's observation (*ibid.* 306), that basic potassium paraoxybenzoate is converted by heat into potassium orthophenoldicarboxylate. (4.) A nearer examination of the product obtained by heating sodium paraoxybenzoate in a stream of carbon dioxide showed the presence of orthophenoldicarboxylic acid, $C^6H^4(OH)(CO^2H)^2$, and oxytrimelic acid, $C^6H^4(OH)(CO^2H)^3$. By conducting the operation very slowly, the end-product was found to contain basic sodium oxytrimesitate only, the reaction taking place as follows:



Potassium paraoxybenzoate, heated to 240° - 250° in a stream of carbon dioxide, is resolved into basic potassium paraoxybenzoate, phenol, and carbon dioxide, small quantities of orthophenoldicarboxylic and oxytrimelic acids being, however, formed at the

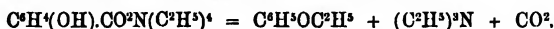
same time, in consequence of the decomposition of the potassium salt of the former acid at high temperatures into basic paraoxybenzoate and carbon dioxide.

The identity of the orthophenoldicarboxylic and oxytrimelic acids obtained above with those obtained from salicylic acid is fully borne out by their characters. The alkaline salts of oxybenzoic acid (meta-) differ from those of the isomeric acids in their behaviour when heated; they yield no basic salts, and only a small amount of impure phenol, the residue becoming carbonised.

Thallous Oxybenzoate, $C^6H^4(OH).CO^2Tl$, prepared by neutralising the acid with thallous carbonate and evaporating the solution, crystallises in colourless shining prisms, easily soluble in hot, less soluble in cold water. Basic thallous oxybenzoate, prepared by heating an aqueous solution of oxybenzoic acid with excess of thallous hydrate, and evaporating the solution, crystallises in yellow prisms more soluble than the neutral salt, and possesses an alkaline reaction.

The basic alkaline oxybenzoates are white hygroscopic powders, which when heated in a stream of carbon dioxide leave a residue containing only oxybenzoic acid.

Tetraphylammonium Salicylate, $C^6H^4(OH).CO^2N(C^2H^5)^4$, prepared by neutralising the aqueous solution of the base with salicylic acid, and evaporating the solution, is a brown, syrupy, highly hygroscopic mass. When heated to 150° , it is resolved into triethylamine and ethyl salicylate. The metoxybenzoate of this base resembles the salicylate; the paraoxybenzoate is, however, resolved at 170° into carbon dioxide, triethylamine, ethylparaoxybenzoate, and phenetol, as follows:



The *oxybenzoates of triethylphenylammonium*, $C^6H^4(OH).CO^2N(C^2H^5)^3(C^2H^5)$, are more stable than those of tetraphylammonium, but are decomposed by heat in a similar manner, yielding diethylphenylamine and the ethyl-ether of the acid.

The *Salicylate and Paraoxybenzoate of Methylamine*, $C^6H^4(OH).CO^2N(CH^3)H^3$, are deliquescent crystalline masses, which are resolved by heat into methylamine, phenol, and carbon dioxide. The metaoxybenzoate, however, yields, when heated, methylamine and oxybenzoic acid.

The *aniline oxybenzoates*, prepared by dissolving equivalent quantities of base and acid in alcohol, and evaporating the solution, are well crystallised compounds, and are decomposed by heat in a similar manner to the methylamine salts, the paraoxybenzoate yielding a small quantity of the anilide.

The three oxybenzoyl-anilides are prepared by heating the aniline salts with PCl^3 or P^2O^5 as crystalline bodies.

Salicyl-anilide crystallises in prisms melting at 132° (134° – 135° , Wanstrat, *Deut. Chem. Ges. Ber.* vi. 336).

Paraoxybenzoyl-anilide crystallises in yellow shining plates, melting at 196° – 197° .

Oxybenzoyl-anilide crystallises in white silky needles, melting at 154° – 155° .

These anilides are all easily soluble in alcohol, and sparingly soluble in water; with the alkali-metals and thallium they form easily soluble compounds by the replacement of the hydrogen in the hydroxyl group by metal, their solutions yielding amorphous precipitates with salts of the heavy metals. Salicyl-anilide differs from the others in giving a violet coloration with ferric chloride.

On the formation of Oxybenzoic Acid (Meta-) together with Salicylic Acid from Orthochlorobenzoic Acid, see p. 284.

Solubility in Water.—H. Ost (*J. pr. Chem.* [2], xvii. 228) has determined the solubility of the three oxybenzoic acids and of benzoic acid in water by filling strong flasks with the hot solutions of the acids, closing them loosely after cooling, and surrounding them with ice for several days, and estimating by titration the amount of acid remaining in solution after the deposition of the crystals. The solubilities at 0° were thus found to be:

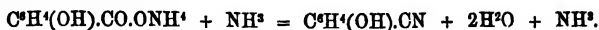
Salicylic	Benzoic	Paraoxybenzoic	Metaoxybenzoic
1 in 1050}			
to 1 in 1100}	1 in 640	1 in 580	1 in 265

All four acids require much longer time for the complete deposition of crystals when the solutions are dilute than when they are concentrated.

Oxidation.—The three monoxybenzoic acids, also protocatechuic acid and gallic acid, when subjected to the action of chromic acid mixture, are oxidised, with violent reaction, to carbon dioxide (J. Remsen, *Chem. News*, xxvii. 213, 277).

Action of Ammonia.—Salicylic and paraoxybenzoic acids, heated with dry ammonia, give first the ammonium salts, which when heated yield phenol and carbon dioxide.

Metaoxybenzoic acid however, when similarly treated, yields oxybenzonitril, according to the equation—



This oxybenzonitril melts at 82° , and is identical with that which Griess obtained from the sulphate of diazocyanbenzene, $\text{C}^6\text{H}^3(\text{CN})\text{N}^2\text{H}^2\text{SO}^4$ (*Ber.* v. 669).

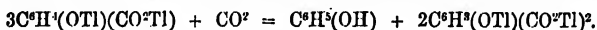
The three isomeric acids show a similar behaviour when distilled with potassium thiocyanate, the metaoxybenzoic acid alone yielding the nitril. This method of preparing the nitril is, however, less easy than the former.

The oxybenzonitril yields, by treatment with sulphuric acid and nitric acid, a mononitrated substitution-compound melting at 182° – 183° , which when boiled with alkalis yields a nitro-oxybenzoic acid (H. J. Smith, *J. pr. Chem.* [2], xvi. 218).

Ortho-oxybenzoic or Salicylic Acid, $\text{C}^6\text{H}^4(\text{OH}).\text{CO}^2\text{H}^4$. Experiments on the action of heat on the normal salicylates, $\text{C}^6\text{H}^4(\text{OH}).\text{CO}^2\text{M}$, have been made by A. v. d. Velden (*J. pr. Chem.* [2], xv. 151), with the following results. All these salts are decomposed into basic salt, phenol, and carbon dioxide, in accordance with the equation established by Kolbe for the sodium-salt, viz.



the salicylates of the heavy metals however partly yield free salicylic acid, and the copper and silver salts are readily decomposed on account of the easy reducibility of the metals which they contain. This reaction, in the case of the potassium salt, as shown by Ost (p. 285), and likewise in that of the rubidium salt, and at a high temperature partly in that of the thallium salt, is attended with the conversion of the salicylic into paraoxybenzoic acid. The thallium salt is at the same time partly converted, like the sodium salt at high temperatures (p. 280), into phenoldicarboxylate:



Normal Thallium Salicylate, $\text{C}^6\text{H}^4(\text{OH}).\text{CO}^2\text{tl}$, prepared with the calculated quantities of salicylic acid and thallium carbonate, is moderately soluble in cold, easily in hot water, has a neutral reaction, and separates on cooling from a hot concentrated solution in thick anhydrous needles. The *basic salt*, $\text{C}^6\text{H}^4(\text{OTl}).\text{CO}^2\text{Tl}$, is precipitated in small, nacreous, faintly-yellowish rhombic plates on mixing a hot solution of the normal salt with the solution of an equivalent quantity of thallium hydroxide. It is nearly insoluble in cold, very slightly soluble in hot water.

Aluminium Salts.—On mixing a solution of normal sodium salicylate with a solution of alum, a white crystalline precipitate is formed which is not always of constant composition, but appears to consist for the most part of *normal aluminium salicylate*, $\text{Al}^3(\text{C}^6\text{H}^3\text{O}^3)^3$. By prolonged standing, and especially by boiling with water, salts richer in aluminium are formed.

Normal Ferric Salicylate, $\text{Fe}^3(\text{C}^6\text{H}^3\text{O}^3)^3$, separates on mixing the normal sodium salt with ferric chloride, as a brown precipitate, which, together with the mother-liquor, quickly acquires the deep violet colour produced on bringing free salicylic acid in contact with ferric chloride. After washing, it forms a brown amorphous body, which yields a violet solution when boiled with water.

Dibromosalicylic Acid, $\text{C}^6\text{H}^2\text{Br}^2(\text{OH}).\text{CO}^2\text{H}$, produced by the action of bromine on salicylic acid, forms colourless needles, which dissolve sparingly in water, easily in alcohol, and melt at 219° . Its solution is coloured violet by ferric chloride. Neither this acid nor monobromosalicylic acid appears to form bimetallic salts (Hübner, *Ber.* x. 1707).

Dichlorosalicylic Acid, $\text{C}^6\text{H}^2\text{Cl}^2(\text{OH}).\text{CO}^2\text{H}$. The modification of this acid, produced by passing the calculated quantity of chlorine into a solution of salicylic acid in acetic acid, is precipitated therefrom in white flocks on addition of water, and may be purified from the monochlorinated acid by conversion into barium salt. It is insoluble in cold, but soluble in boiling water; dissolves easily in cold alcohol, and separates from the solution on spontaneous evaporation in stellate groups of colourless needles. It melts at 214° , and sublimes with partial decomposition. Ferric chloride produces a fine violet colour in its aqueous solution. The *barium salt*, $[\text{C}^6\text{H}^2\text{Cl}^2(\text{OH}).\text{CO}^2]^2\text{Ba} + 3\frac{1}{2}\text{H}^2\text{O}$, is insoluble in water, easily soluble in boiling alcohol, and crystallises therefrom in large colourless needles. The *potassium salt*, $\text{C}^6\text{H}^2\text{Cl}^2(\text{OH}).\text{CO}^2\text{K}$, crystallises from its concentrated aqueous solution in white needles. The *sodium salt*, $\text{C}^6\text{H}^2\text{Cl}^2(\text{OH}).\text{CO}^2\text{Na}$, forms easily soluble needles; the *magnesium salt*, $[\text{C}^6\text{H}^2\text{Cl}^2(\text{OH}).\text{CO}^2]^2\text{Mg}$, very soluble crystals. The *lead salt*, $\text{C}^6\text{H}^2\text{Cl}^2\text{OPbCO}^2$, is a white insoluble precipitate; so likewise is the *silver salt*. The

copper salt forms small brown soluble crystals. The *ethylic ether*, $C^6H^2Cl^2(OH)CO^2C^2H^5$, crystallises from alcohol in needles melting at 47° , and forms a potassium salt, $C^6H^2Cl^2(OK)CO^2C^2H^5$. The acid treated with nitric acid yields a soluble nitro-derivative (E. F. Smith, *Amer. Phil. Soc. Proc.* xvii. 68).

Nitrosalicylic Acids. Two mononitrosalicylic acids, $C^6H^3(NO^2)(OH)CO^2H$, obtained by direct nitration of salicylic acid, were described by Hübner in 1874 (*Ber.* vii. 1320), and distinguished as *ortho*- and *para*-nitrosalicylic acids, because when heated they yielded respectively *ortho*- and *para*-nitrophenol (p. 281). In a subsequent paper (*ibid.* x. 1697) they are named α - and β -*orthohydroxymetanitrobenzoic acid*, or more shortly α - and β -*nitrosalicylic acid*. These two acids may be represented by the following formulæ,



the α -modification being evidently resolvable into CO^2 and *o*-nitrophenol, the β -modification into CO^2 and *p*-nitrophenol.

α -Nitrosalicylic acid yields a diethyl-compound (p. 282), convertible by treatment with alcoholic ammonia into

α -*Orthamidometanitrobenzoic acid*, $C^6H^3.NH^2.NO^2.COOH$, which forms very long delicate golden-yellow needles, melting at 263° . Its *barium salt* forms brownish-yellow crystals. The acid is converted by treatment with nitrous acid into a white diazo-compound, and this, when treated with alcohol, yields a metanitrobenzoic acid which melts at 140° , and is converted by reduction with tin and hydrochloric acid into an amido-acid melting at 173° . This shows that the nitro-group in the acid occupies the meta-position in relation to the carboxyl-group, as the name implies.

Together with the foregoing amidonitrobenzoic acid, there is formed an *amide*, $C^6H^3.NO^2.NH^2.CONH^2$, which crystallises in long, colourless, sparingly soluble needles melting at 225° . Solutions of this substance produce a deep-red colour with ferric chloride. It forms colourless compounds with nitric and hydrochloric acids.

β -Nitrosalicylic acid, when pure, melts at 131° , not at 145° , as formerly stated.

β -*Orthamidometanitrobenzoic acid*, obtained in the same manner as the α -compound (see above), forms long yellow needles melting at 204° , and volatilises easily with steam. It is converted by treatment with nitrous acid and alcohol into metanitrobenzoic acid melting at 142° , and yielding, by reduction with tin and hydrochloric acid, an amido-acid melting at 174° . The *amide*, formed together with the nitro-acid, melts at 109° .

Sulphonic acids.— α -Nitrosalicylic acid is converted by heating with fuming sulphuric acid into a sulphonic acid, $C^6H^2(OH)(NO^2)(COOH)SO^2H$, the calcium and barium salts of which crystallise in hair-like needles. This acid yields by reduction the corresponding *amido-acid*, $C^6H^2(OH)(NH^2)(SO^2H)COOH + H^2O$.

α -*Metamidosalicylic acid*, when heated with fuming sulphuric acid, yields colourless needles of the sulphonic acid, $C^6H^2(OH)(NH^2)(SO^2H)COOH + 3H^2O$, the calcium salt of which crystallises with 5 mols. of water.

Dinitrosalicylic acid.—The two mononitro-salicylic acids above described are converted by fuming nitric acid into the same dinitrosalicylic acid, $C^6.CO^2H.OH.NO^2.H.NO^2.H$, which crystallises in thick shining prisms and tables containing 1 mol. H^2O , and becoming turbid on drying. It is but slightly soluble in cold water, still less in dilute acids. The aqueous solution is coloured red by ferric chloride. The dehydrated acid melts at 173° . The *dipotassium salt*, $C^6H^2(NO^2)^2OK.CO^2K + H^2O$, forms dark red needles having a velvety lustre. The *monammonium salt*, $C^6H^2(NO^2)^2OH.CO^2NH^4$, crystallises from the solution of the acid in concentrated aqueous ammonia in fiery-yellow needles. The *monobarium salt*, $C^6H^2(NO^2)^2O(CO^2)Ba + 3H^2O$, formed by neutralising the acid with barium carbonate, crystallises in very small soft needles. The *monocalcium salt*, $C^6H^2(NO^2)^2O(CO^2)Ca + 1\frac{1}{2}(? 2\frac{1}{2})H^2O$, prepared like the barium salt, crystallises in nodular groups of small needles, somewhat more soluble than the barium salt. The *monoplumbic salt*, $C^6H^2(NO^2)^2O(CO^2)Pb + 3H^2O$, is a light yellow precipitate very sparingly soluble in water, but moderately soluble in hot dilute acetic acid, from which it crystallises in very brilliant light yellow needles. The *ethylic ether* melts at 99° – 100° (H. Behagel von Adlerskron, *Inaugural dissertation*, Göttingen, 1877; *Ber.* x. 1700).

Paraoxybenzoic Acid, $C^6.CO^2H.H.H.OH.H^2$. An elaborate investigation of the formation, properties, and derivatives of this acid has been made by O. Hart-

mann (*J. pr. Chem.* [2], xvi. 35). In preparing it from potassium phenate, it is advisable first to heat the latter in contact with the air, or better in a stream of hydrogen, and then to pass carbon dioxide gradually into it. The product thus obtained amounts to 80, or, if very pure potassium phenate be used, to 90 per cent. of the theoretical amount. If, on the other hand, the carbon dioxide be passed in before the potassium phenate is heated, or if the retort filled with the gas be suddenly heated to 180° , the mass becomes viscid, and the greater part of the potassium phenate is prevented from coming in contact with the carbon dioxide. On dissolving the product in water and adding hydrochloric acid, the paraoxybenzoic acid is precipitated as a brown crystalline powder, which may be purified by boiling its aqueous solution with hydrochloric acid, or better with animal charcoal. The purification may also be effected through the medium of the ethylic ether. Traces of salicylic acid may be removed by crystallisation from chloroform.

Paraoxybenzoic acid crystallises well from dilute alcohol. The crystals, according to v. Rousch's investigation, are monoclinic, with the axial ratio $a : b : c = 1.3703 : 1 : 1.10224$, and the angle $ac = 105^{\circ} 26'$.

The following salts were prepared by neutralising the aqueous acid with the corresponding carbonates. The *sodium salt*, $C^6H^4(OH)CO^2Na + 5H^2O$, is obtained by crystallisation from a very strong solution at as low a temperature as possible, in slightly brown translucent plates which effloresce with great facility. The *potassium salt*, $C^6H^4(OH)CO^2K + 3H^2O$, obtained in like manner, is permanent in the air. The *ammonium salt* crystallises with 1 mol. water; its solution gives off ammonia on evaporation, so that it must be neutralised before crystallisation, which takes place only from very strong solutions and at low temperatures. It forms large, slowly efflorescing prisms an inch in length. The *calcium salt*, $[C^6H^4(OH)CO^2]_2Ca + 4H^2O$, forms slender needles; the *barium salt* either flat needles with 1 mol. H^2O , or well-developed acute rhombohedrons with basal pinacoid, containing $2H^2O$. The *strontium salt* mostly forms slender needles, less frequently moderately large crystals. The *cadmium salt* crystallises from hot concentrated solutions in needles with $4H^2O$; from dilute solutions in granules with $6H^2O$. The former salt changes into the latter when left for some time in the mother-liquor. The *zinc salt* forms granular crystals containing $8H^2O$. The *ethylic ether*, $C^6H^4(OH)CO^2C^2H^5$, melts at 116° , also when heated under water, in which it dissolves in small quantity at the boiling heat. It is insoluble in carbon sulphide, only slightly soluble in chloroform and benzene, but dissolves readily in alcohol and ether.

Paraoxybenzamide, $C^6H^4(OH)CO.NH^2 + H^2O$, produced by heating the ether just described with aqueous ammonia at 130° , crystallises from water in needles, and is quickly dehydrated at 100° , slowly over sulphuric acid; dissolves easily in alcohol and in hot water, sparingly in ether and in cold water; is nearly insoluble in chloroform, carbon sulphide, and benzene; melts at 162° . It combines both with bases and with acids. *Sodium-paraoxybenzamide*, $C^6H^4(ONa)CONH^2$, is thrown down by caustic soda from an alcoholic solution of the amide as a white precipitate insoluble in ether; from solution in alcohol it separates in crystals. *Dihydrochloride of Paraoxybenzamide*, $C^6H^4(OH)CONH^2.2HCl$, formed by passing hydrogen chloride over the amide, is easily soluble in water.

Paraoxybenzonitril, or *Paracyanphenol*, $C^6.CN.H.H.(OH).H^2$, formed from the amide, or better from the ammonia salt by rapid distillation with phosphorus pentoxide, crystallises from hot water in beautifully iridescent laminae of the thickness of a sheet of paper; by slower formation in tablets, which according to v. Rousch are orthorhombic, exhibiting the combination $\infty P . P . 0P$. Angle $\infty P : \infty P = 81^{\circ} 4'$; $0P : P = 74^{\circ} 12'$. Hence $a : b : c = 0.8551 : 1 : 2.308$. Plane of optic axes ac ; first median line e . Dispersion very remarkable $\rho > \nu$. Angle of optic axes for red light about 49° in air. The crystals are optically negative. The nitril dissolves sparingly in cold, more freely in hot water, easily in alcohol, ether, and chloroform; it has a sweet taste, with burning after-taste. Soda-ley added to its ethereal solution throws down the sodium-compound, $C^6H^4(ONa)CN$ (dried at 100°), which crystallises from alcohol as well as from water, in the latter case with water of crystallisation.

On *Dinitromethylparaoxybenzoic* or *Dinitranisic acid*, see Salkowsky & Rudolph, (p. 287).

Aldehydo-oxybenzoic Acids, $C^6H^4O^4 = C^6H^2(COH)(OH)(COOH)$. Reimer & Tiemann in 1876 obtained ortho- and para-aldehydo-salicylic and ortho-aldehydo-paraoxybenzoic acids, by the action of chloroform on *o*- and *p*-oxybenzoic acids in alkaline solution (p. 288), and the following additional details respecting these acids are given by the same authors in a subsequent communication (*Ber.* x. 1576).

The best yield is obtained by dissolving 30 grams of salicylic (or paraoxybenzoic) acid in 100 c.c. of caustic soda-solution of sp. gr. 1.35 (containing about 43 grams of sodium hydroxide), and cocolating with 5-10 grams of chloroform, further quantities of the last substance being from time to time added (20-25 grams in half an hour). When a little chloroform condenses and drops back, more caustic soda-solution is added, so that in the course of 4 to 5 hours about 150 c.c. of the soda-solution and 45-46 grams of chloroform have been used altogether: no appreciable increase in the yield is noticed after this stage.

The resulting deep-red liquid is cautiously neutralised with hydrochloric acid, whereby a dark resinous decomposition-product is thrown down: the filtrate is strongly acidulated with hydrochloric acid, and the resulting liquid (containing in suspension a white precipitate) is agitated with ether; the concentrated ethereal extract is then shaken with 100 c.c. of solution of sodium-hydrogen sulphite of sp. gr. 1.35, diluted with 40-50 c.c. of water, which quantity suffices to take up all the aldehydo-bodies found. By means of sulphuric acid and steam (40 grams concentrated acid diluted with 40 c.c. of water) the sulphite compounds are decomposed, the whole being thrown on a filter after cooling to 60°. If paraoxybenzoic acid is used in the first instance, *ortho-aldehydo-paraoxybenzoic acid* remains on the filter, a little more of this acid being contained in the filtrate, together with a little *paraoxybenzoic aldehyde*; the yield of the aldehydo-acid is about 20 per cent. of the paraoxybenzoic acid employed. If salicylic acid was originally employed, *para-aldehydo-salicylic acid* remains on the filter, the filtrate containing small quantities of the same, together with *ortho-aldehydo-salicylic acid*. *Salicylic aldehyde* is also produced in small quantity when the soda-solution originally used was more dilute than that recommended, and especially if the mixture was not heated to a higher temperature than the boiling point of chloroform, a large quantity of that substance being added at first: this product is easily isolated by distillation with steam, the quantity not exceeding 1 or 2 per cent. of the salicylic acid used: it is possibly formed by the splitting up of the salicylic acid into phenol and carbon dioxide, the former being then aldehydated; or it may be produced by the decomposition of the *ortho-aldehydo-salicylic acid*; or, again, and more probably, it may result from a direct exchange of carboxyl for aldy (the group COH characteristic of aldehydes).

To separate the *ortho*- and *para*-aldehydo-salicylic acids, the method formerly described (methodical crystallisation) does not suffice, traces of the *para*-acid being always retained by the *ortho*-acid thus prepared. The following process answers well:—The solution of the mixed acids is shaken with ether, the ethereal extract evaporated, and the residue dissolved in considerably diluted ammonia-liquor: copper sulphate solution is then added, and sufficient ammonia to dissolve a portion of the precipitate with a blue colour; the whole is then heated to boiling, when almost the whole of the *ortho*-acid separates as a basic copper salt of a bright green colour, con-

taining when dried at 100°, $\text{C}^6\text{H}^3\begin{matrix} \diagup \text{CO}_2 \\ \text{O} \\ \diagdown \text{COH} \end{matrix} \text{Cu}$; on treatment with dilute hydrochloric

acid, this salt yields pure *ortho-aldehydo-salicylic acid*, crystallising from water in fine interlaced needles resembling salicylic acid, and melting at 179° when perfectly pure (166° was given as the melting point in a former paper): by careful heating it can be sublimed unchanged, but if quickly heated to 220° in the fused state, it splits up into carbon dioxide and salicylic aldehyde: when crystallised it is represented by the formula $\text{C}^6\text{H}^4\text{O}^4\text{H}^2\text{O}$; the crystals becoming anhydrous at 100°. Alcoholic solutions of the acid exhibit a faint bluish-violet fluorescence; in caustic soda it dissolves with a yellow colour. Ferric chloride strikes a red tint, and sodium carbonate dissolves the acid with effervescence.

Two classes of salts are formed by each one of the three aldehydo-acids, viz., normal salts, and basic salts in which the phenolic hydrogen is also replaced; the points at which the normal salts are formed with alkalis and the two salicylic derivatives are easily determined by means of litmus, a red coloration being given to the litmus as long as the amount of alkali added is less than that requisite to form the normal salt, and a blue with the slightest excess: with the paraoxybenzoic derivative, however, the point of neutrality cannot be thus determined, as the litmus becomes green before the amount of alkali requisite to form the neutral salt is added; further addition of alkali deepens the green, but there is no characteristic colour change marking the point of neutrality. The alkali-salts of all these acids are very soluble, and crystallise only from extremely concentrated solutions; the normal salts of the two salicylic derivatives are colourless by transmitted light, appearing to possess a green fluorescence with reflected light; traces of excess of alkali give a yellow coloration. The neutral and ammoniacal solutions (concentration about 1:50) exhibit the reactions given in the following table:

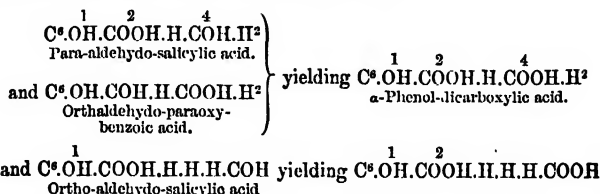
Reactions of Aldehyde-oxybenzoic acids.

Reagents	Ortho-aldehyde-salicylic acid			Para-aldehyde-salicylic acid			Ortho-aldehyde-paraoxybenzoic acid		
	Neutral solution	Ammoniacal solution		Neutral solution	Ammoniacal solution		Neutral solution	Ammoniacal solution	
Calcium Chloride.	—	Flocculent white basic calcium salt.		—	Crystalline white basic calcium salt.		—	—	
Barium Chloride.	—	White granulo-crystalline basic barium salt.		—	White granulo-crystalline basic barium salt.		—	Flocculent white basic barium salt, separating only on heating.	
Silver Nitrate	White granular silver salt, dissolving without alteration in boiling water, and separating therefrom on cooling in stellate groups of scales.	The normal silver salt dissolves in excess of ammonia; the ammoniacal solution blackens on prolonged heating.		Granular white silver salt, dissolving in a large quantity of boiling water, and separating on cooling in tufts of microscopic needles.	The normal silver salt dissolves in excess of ammonia, forming a solution which does not blacken when heated.		Gelatinous silver salt, soluble in excess of ammonia. The solution does not blacken when heated.	The ammoniacal solution of the normal silver salt blackens easily when heated.	
Copper Sulphate.	Light green crystalline copper salt, soluble with green colour in excess of ammonia.	Basic gelatinous copper salt, dissolving, when recently precipitated, in excess of ammonia, the solution on standing, or more quickly when heated, depositing a granular salt.		Crystalline copper salt, separating after long standing in needles.	Flocculent basic copper salt, easily soluble in excess of ammonia. The solution does not become turbid when heated.		Hydrated green copper salt, becoming crystalline when heated.	Gelatinous basic copper salt, easily soluble in excess of ammonia; the solution does not become turbid when heated.	
Lead Acetate*	Bulky white lead salt.	Bulky basic lead salt.		Dense white lead salt.	Bulky white basic lead salt.		Bulky white lead salt.	Bulky white basic lead salt.	
	Soluble in acetic acid.			Easily soluble in acetic acid.			Easily soluble in acetic acid.		

* Aqueous solutions of the three aldehyde-oxy-acids likewise give slight white precipitates with lead acetate.

Ortho-aldehydro-salicylic acid dissolves in 1500–1600 pts. of water at 23°–25°, and in 15–16 pts. at 100°; para-aldehydro-salicylic acid in 2600–2700 pts. at 25°, and in 145–150 pts. at 100°; ortho-aldehydro-paraoxybenzoic acid is slightly more soluble in cold water than the latter.

By fusion, with potash, these three aldehyde-acids are readily converted into phenol-dicarboxylic acids, $C^6H^2(OH)(COOH)_2$.



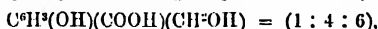
See PHENOL-CARBOXYLIC ACIDS.

Reduction of Aldehyde-oxybenzoic Acids to Alcoholic Acids (Reimer, Ber. ix. 790).—This transformation is effected by treating the aldehyde-acids with sodium-amalgam: 1 pt. of the aldehyde-acid is suspended in about 10 pts. of water, and treated gradually with 50 pts. of 3 per cent. sodium-amalgam. The reduction of the aldehyde under these circumstances is nearly complete, but resinous products are invariably formed at the same time. Hydrochloric acid is then added in slight excess, and the alcoholic acid, mixed with resin, is extracted by agitation with ether. The separation of the resin is effected, either by dissolving the mixture in ammonia, adding barium chloride, and leaving the solution for some weeks, when the resin separates completely in combination with barium; or by acidifying the ammoniacal solution with hydrochloric acid, quickly filtering off the resin mixed with some acid, and allowing the rest of the acid to separate spontaneously.

Paraoxymethyl-salicylic acid, $C^6H^2(OH)(COOH)(CH^2OH) = (1 : 2 : 4)$, from para-aldehydosalicylic acid, crystallises from ether in long prisms containing 1 mol. water of crystallisation. It is sparingly soluble in water, more so in alcohol and ether. It decomposes at 160°, and is resinised by warm mineral acids. Permanganate solution converts this acid in the cold into α -oxyisophthalic acid; when heated with potassium dichromate it is oxidised to para-aldehydosalicylic acid.

Ortho-oxyethylsalicylic acid, $C^6H^2(OH)(COOH)(CH^2OH) = (1 : 2 : 6)$, is precipitated as an oil, which solidifies to crystals, melting at 142°. A solution of this acid in water, especially in presence of free mineral acid, is resinised by heat. An ammoniacal solution of it, heated with potassic dichromate, gives again the corresponding aldehyde-acid.

Ortho-oxyethylsalicylic acid (saligeninpara-carbonsäure):



obtained by reduction of ortho-aldehydro-oxydracyle acid, is much more stable than its isomerides, and does not melt at 270°. It is not coloured either by sulphuric acid or by ferric chloride. With the latter reagent its isomerides, mentioned above, give intense violet colours.

OXYBENZOIC ALDEHYDES or OXYBENZALDEHYDES, $C^6H^4O^2 = OH.C^6H^4.CO.H$. Two of these compounds, viz. salicyl-aldehyde, $[OH : COH = 1 : 2]$, and paraoxybenzaldehyde, $[1 : 4]$, produced simultaneously by the action of chloroform on a strongly alkaline solution of phenol, have already been described (p. 303). According to T. L. Phipson (*Compt. rend.* lxxxiv. 1034), when salicylic acid (1 gram) is heated with water (30–40 g.) and fuming nitric acid (5 c.c.) there is formed, together with nitro-salicylic acid, a very considerable quantity of salicyl-aldehyde due to the action of nitrous acid, which may be separated from the red liquid, after the nitrosalicylic acid has crystallised out, by agitation with ether. Salicylaldehyde is also formed, together with nitrosalicylic acid, when salicylic acid is heated with a solution of potassium nitrite.

On the conversion of Salicylaldehyde into *Coumaric Acid* and *Coumarin*, see pp. 574, 575.

Paraoxybenzaldehyde, $C^6.CO.H.H.H.OH.H^2$.—The following derivatives of this compound have been prepared and examined by Herzfeld (*Ber.* x. 1267, 2196):

Chloroparaoxybenzaldehyde, $C^6H^3Cl(OH)(COH)$, is formed in theoretical quantity by passing chlorine gas over the dry oxyaldehyde, and crystallises in long silky needles, which melt at 148°–149°, and are freely soluble in water, alcohol, and ether.

With the alkalis it forms salts, which crystallise in long needles, and are soluble in water. It absorbs ammonia in the proportion of 1 : 2 mols., and differs in this respect from paraoxybenzaldehyde, 1 mol. of which unites with 1 mol. of NH_3 . The compound thus formed crystallises from absolute alcohol in beautiful needles. The aqueous solutions of paraoxybenzaldehyde and of its chlorine-compound give a violet reaction with ferric chloride.

The corresponding *bromine-compound*, $\text{C}^6\text{H}^3\text{Br}.\text{OH}.\text{COH}$ (m. p. 179°), is formed when the dilute alcoholic solution of paraoxybenzaldehyde is allowed to absorb bromine vapour. It resembles, in all respects, both the latter compound and its chlorine-derivative, with the exception that its aqueous solution is not coloured by ferric chloride.

The *iodine-compound*, $\text{C}^6\text{H}^3\text{I}.\text{OH}.\text{COH}$ (m. p. 198°), is formed by heating the dilute alcoholic solution of paraoxybenzaldehyde with iodine for some hours. By the action of potassium hydrate at a high temperature (160° – 170°) upon this body, it is converted into protocatechuic acid.

Nitroparaoxybenzaldehyde, $\text{C}^6\text{H}^3\text{OH}(\text{NO}^2)\text{COH}$, is formed by dropping strong nitric acid into a mixture of 3 pts. of paraoxybenzaldehyde with 20 pts. of strong sulphuric acid. On diluting with water it is deposited as a golden-yellow mass, which crystallises in yellow needles from its aqueous solution. It melts at 139° – 140° , dissolves easily in alcohol and benzene, sparingly in ether and chloroform, sublimes entirely on heating, and volatilises with steam. It forms a crystalline, sparingly soluble compound with acid sodium sulphite, and produces a transient reddish coloration with ferric chloride.

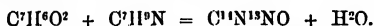
Paraoxybenzaldehyde absorbs 13.46 per cent. (= 1 mol.) of dry ammonia gas, forming with it an oily body, which, on exposure to air, gradually gives off ammonia, and leaves the unaltered aldehyde.

Salicylic aldehyde likewise absorbs 1 mol. of ammonia, forming a compound which is resolved by heat into water, ammonia, and hydrosalicylamide.

Paraoxybenzaldehyde in ethereal solution reacts with aniline to form a pale-yellow crystalline body, which melts at 190° – 191° , and dissolves easily in alcohol and ether, sparingly in benzene and chloroform. From the analysis of the body it appears to be formed by the following reaction:



Paraoxybenzaldehyde also unites with paratoluidine, with elimination of water, according to the equation:



The product of the reaction is an orange-coloured body, which crystallises from its alcoholic solution in four-sided plates, melting at 213° . The inverse reaction is determined by boiling the compound with dilute acids or alkalis.

Paraoxybenzyl alcohol, $\text{C}^6\text{H}^4(\text{OH})\text{CH}_2\text{OH}$, is formed by the action of sodium-amalgam on paraoxybenzaldehyde. It is a solid crystalline substance, melting at 197.5° , soluble in water, alcohol, and ether, and sparingly in benzene and chloroform. It gives a transient blue coloration with ferric chloride, and is coloured brown by strong sulphuric acid.

Hydroparaoxybenzoin, $\text{C}^{14}\text{H}^{14}\text{O}^4$, is produced on treating with sodium-amalgam a mixture of paraoxybenzaldehyde with more than 10 pts. of water. It is thrown down, on neutralising the liquid, as a white crystalline substance, melting at 222° , easily soluble in boiling water, less easily in alcohol, benzene, and chloroform.

OXYBENZOTRISULPHONIC ACID, $\text{C}^6\text{H}^3\text{S}^3\text{O}^{12} = \text{C}^6\text{H}(\text{OH})(\text{SO}^3\text{H})^2\text{COOH}$.

Trisulphoxybenzoic acid. This acid is prepared by heating a solution of 10 grams of benzoic acid in 20 grams of sulphuric acid, with 15 grams of phosphorus pentoxide and 20 grams of sulphur trioxide in sealed tubes at 250° for five hours. The contents of the tubes are boiled with water to expel sulphur dioxide, and the sulphuric and phosphoric acids are removed by the addition of calcium carbonate. To obtain the free acid, basic acetate of lead is added to the filtrate, and the precipitated lead salt decomposed by sulphuretted hydrogen.

Trisulpho-oxybenzoic acid is a yellow syrupy hygroscopic liquid, which, after drying at 100° , has the composition $\text{C}^6\text{H}^3\text{S}^3\text{O}^{12} + 4\text{H}_2\text{O}$. Both the acid and its salts produce, with a drop of ferric chloride, an intense carmine coloration, which disappears on the addition of sodium carbonate.

The *basic lead salt*, $(\text{C}^6\text{H}^3\text{S}^3\text{O}^{12})_2\text{Pb}^3 + 6\text{H}_2\text{O}$, forms white opaque needle-shaped crystals, which lose their water of crystallisation at 235° . By the partial decomposition of this compound with sulphuretted hydrogen the *normal lead salt*, $\text{C}^6\text{H}^3\text{S}^3\text{O}^{12}\text{Pb}^2 + 8\text{H}_2\text{O}$, is obtained. *Basic potassium trisulpho-oxybenzoate*,

$C^7H^5O^{12}K^5 + 2H^2O$, crystallises in monoclinic prisms; the normal salt, $C^7H^5S^3O^{12}K^4 + 2H^2O$, separates out on addition of alcohol to trisulpho-oxybenzoic acid which has been nearly neutralised with potassium carbonate.

The barium salt, $C^7H^5S^3O^{12}Ba^2$, is decomposed by long-continued heating at 100° , or by boiling with barium carbonate, barium sulphate and barium disulpho-oxybenzoate, $(C^7H^5S^2O^9)^2Ba^2 + 8H^2O$, being formed in the latter case.

Trisulpho-oxybenzoic acid appears to be completely destroyed by fusion with potash, as only traces of pyrogallie and oxalic acids could be detected in the fused product. Attempts to replace the hydrogen in this acid by bromine were unsuccessful, the acid splitting up into monobromodisulpho- and dibromomonosulpho-benzoic acids (Kretschy, *Ber.* xi. 858).

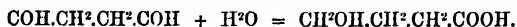
OXYBENZYL ALCOHOL, $C^7H^8O^2 = C^6H^4OH.CH^2OH$ [OH : $CH^2OH = 1 : 3$]. *Benzyl Glycol* (A. v. d. Velden, *J. pr. Chem.* [2], xv. 151).—This alcohol is formed, together with other products, by the action of sodium-amalgam on metaoxybenzoic acid in acid solution; in alkaline solution no reduction takes place. To prepare it oxybenzoic acid in moderate quantity is covered with water in a flat-bottomed flask, and about five times its quantity of 4 per cent. sodium-amalgam is gradually added, care being taken that the temperature of the mixture does not rise above 60° . When the action is over, the product is shaken up with ether, the residue left after evaporation of the ether is treated with water and calcium carbonate, and the filtered liquid is again exhausted with ether. The pure alcohol freed from the solvent by spontaneous evaporation, and left in a vacuum over sulphuric acid, solidifies gradually to a white crystalline mass. It melts at 67° ; boils, with partial decomposition, at about 300° ; dissolves slowly in cold, easily in hot water, easily also in alcohol and ether, sparingly in chloroform. With oxidising agents (chromic acid, nitric acid, permanganate), it does not yield any definite products of oxidation; melting potash converts it into meta-oxybenzoic acid (m. p. 200°); alcoholic potash does not act upon it; neither is it attacked by potassium or sodium.

Oxybenzyl Acetates.—The normal ether, $C^6H^4OH.CH^2.OC^2H^3O$, is obtained by the action of glacial acetic acid and sulphuric acid on oxybenzyl alcohol, as an oil which solidifies on drying to a radiate yellow mass. It has a pleasant aromatic odour, melts at 56° , and boils with partial decomposition at 295° – 302° . It is insoluble in water, but dissolves readily in alcohol and ether, and, like the alcohol, gives a violet-blue coloration with ferric chloride.

The acid acetate, $C^6H^4(OC^2H^3O).CH^2.OC^2H^3O$, is obtained by heating the alcohol to 160° with excess of acetic anhydride, as a liquid which solidifies at -18° . It has a pungent odour, boils at about 290° , is insoluble in water, but dissolves in alcohol and ether.

Para-oxybenzyl alcohol, [OH : $CH^2OH = 1 : 4$], formed by the action of sodium-amalgam on paraoxybenzaldehyde, is a solid body, melting at 197.5° , soluble in water, alcohol, and ether, sparingly soluble in benzene and chloroform; gives a violet-blue colour with ferric chloride.

OXYBUTYRIC ACIDS, $C^4H^6O^3 = C^3H^4(OH).CO^2H$. The normal acid, $CH^2OH.CH^2.CH^2.COOH$, is formed by heating succinic aldehyde with water and lime or baryta:

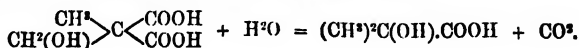


It is crystalline; forms deliquescent calcium and barium salts; is converted by oxidation into succinic acid (A. Saytzeff, *Ber.* vi. 1255).

On α -Oxybutyric Acid, see p. 364.

β -Oxybutyric Acid, $CH^3.CH(OH).CH^2.COOH$ (vi. 891), is formed by oxidation of aldol, $CH^3.CH(OH).CH^2.CHO$, with moist silver oxide. Its zinc salt is easily soluble in water and in alcohol, and crystallises indistinctly; its barium salt also dissolves easily in water and in alcohol, but is uncrystallisable, and is precipitated by ether from its alcoholic solution in flocks; the sodium salt crystallises from solution in alcohol (Wurtz, *Compt. rend.* lxxvi. 1165). The same acid is formed by saponification of the ethyl salt of the chlorobutyric acid obtained by passing chlorine into fermentation butyric acid (Balbiano, *Gazz. chim. ital.* 1878, 90).

α -Oxyisobutyric acid, $(CH^3)^2COH.COOH$, originally produced by the action of moist silver oxide on bromoisobutyric acid, and by that of hydrocyanic and hydrochloric acid on acetone (vi. 891), is also formed by the action of the same acids on propionic aldehyde (p. 364), and by boiling a solution of β -oxyisoprotartaric acid neutralised with baryta-water (Demarçay, *Compt. rend.* lxxxii. 1337):



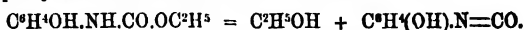
It appears also to be contained in the mother-liquors of the preparation of β -isopyrotartaric or dimethylmalonic acid (p. 1259).

OXYCAMPIC ACID, $C^{10}H^{16}O^3$. See CAMPIC ACID (p. 372).

OXYCAMPHORONIC ACID, $C^9H^{12}O^4$ (vii. 238). On the crystalline form of this acid, see V. v. Zepharovich (*Wien. Akad. Ber.* lxxiii. 1 Abth; *Zeitschr. Kryst.* i. 220; *Jahresb. f. Chem.* 1877, 640).

OXYCAPROIC ACID, $C^6H^{12}O^3$. An acid of this composition, probably $CH^3.CH^2.CH^2.CH^2.CHOH.COOH$, obtained by oxidation of fermentation caproic acid, crystallises in laminae melting at 57° . Its silver, zinc, cadmium, and barium salts are very slightly soluble, and are deposited from their solutions in the amorphous state. By oxidation, it yields carbon dioxide, a valeric acid, and an aldehyde (N. Ley, *Ber.* x. 230). See also LACTIC ACID (p. 1179).

OXYCARBANIL, $CO=N.C^6H^4.OH$, is formed, together with alcohol, by heating methoxyphenylurethane to 200° :



It crystallises from water in needles having a faint red colour; melts at 136° – 138° ; dissolves more freely in alcohol than in ether, easily in alkaline liquids; the solution in potash blackens when boiled. The compound is not attacked by ammonia or hydrochloric acid. The silver salt, $CO=N.C^6H^4.OAg$, is a precipitate resembling silver chloride. Oxycarbanil is not attacked by gaseous or alcoholic ammonia, but when heated to 160° with aqueous ammonia it is decomposed, with formation of amidophenol (Groenock, *Ber.* ix. 1554).

OXYCHOLESTENIC or **OXYCHOLESTERIC ACID**, $C^{26}H^{42}O^3$. A monobasic acid formed, together with cholestenic acid, $C^{26}H^{42}O^4$, also monobasic, and dioxcholestenic acid, bibasic, by oxidation of cholesterol with permanganate (p. 455).

OXYCHRYSAZIN, $C^{14}H^{18}O^3 = C^{14}H^3(OH)^3O^2$. See ANTHRAQUINONES (TRIOXY-), (p. 113).

OXYCINCHOMERONIC ACID, $C^{11}H^8N^2O^8$. } See CINCHONINE (p. 483).

OXYCINCHONINE, $C^{20}H^{24}N^2O^2$.

OXYCITRACONIC ACID, $C^8H^8O^3$. See CITRIC ACIDS (PYRO-), (p. 515).

OXYCITRIC ACID, $C^6H^8O^8$. See CITRIC ACID (p. 510).

OXYCOLOPHTHALIN, $C^{11}H^8O$. A product of oxidation of colophthalin, $C^{11}H^{10}$, a hydrocarbon found by P. Curie (*Chem. News*, xxx. 189) among the products of the dry distillation of colophony.

OXYCOUMARIN, $C^9H^6O^3 = C^8H^3(OH) \begin{array}{c} \text{CH=CH-CO} \\ \diagup \quad \diagdown \\ \text{ } \end{array} \begin{array}{c} \text{ } \\ \text{ } \\ \text{O} \end{array}$. The acetyl-derivative

of this compound, $C^9H^3(OC^2H^3O) \begin{array}{c} \text{CH=CH-CO} \\ \diagup \quad \diagdown \\ \text{ } \end{array} \begin{array}{c} \text{ } \\ \text{ } \\ \text{O} \end{array}$, is formed on heating resorcy-

aldehyde, $C^6H^3(OH)^2COH$, with 1 pt. sodium acetate and 3 to 5 pts. acetic anhydride. It crystallises from water in large faintly yellow prisms melting at 140° ; distils undecomposed; dissolves but sparingly in water even when hot, easily in alcohol and in ether. The aqueous solution exhibits a splendid blue fluorescence, but does not give any colour-reaction with ferric chloride. It is not attacked by alkalis or alkaline carbonates in the cold, but dissolves when heated, forming a solution from which ether extracts oxycoumarin. This substance, after purification, crystallises in small white needles, which dissolve in water (the solution is coloured brown-red by ferric chloride), and decompose without melting at 200° .

Oxycoumarin and its acetyl-derivative have the same composition as β -umbelliferone and β -acetyl-umbelliferone; but whether they are identical with these latter is a point not yet determined (Tiemann & Lewy, *Ber.* x. 2210).

OXYDIBENZYL SULPHONIC ACID, $C^{14}H^{13}(OH)(SO^3H)$, is obtained by fusing potassium dibenzylsulphonate (p. 322) with potash, and precipitating the solution of the melt with hydrochloric acid (Kud., *Ber.* vi. 953).

OXY-DIIMIDO-DIAMIDO-DIISATIN, $C^{14}H^4(NH)^2(NH^2)^2N^2O^3$. See ISATIN (p. 1125).

OXYFLUORESCEIN and **OXYGALLEIN**. See OXYPTHALIC ACID under PHTHALIC ACIDS.

OXYGEN. On the Molecular Relations of Oxygen, see GASES (p. 848). On its Diffusion Relations (pp. 848, 850). Transpiration and Friction-coefficient (pp. 851, 852). Compressibility and Deviation from the Boyle-Mariotte Law (p. 856). Liquefaction and Solidification (p. 857).

On the influence of the position of the Oxygen-atom on the Boiling Point of Oxygenated Carbon-compounds, see HEAT (p. 945).

On the Heat of Combination of Oxygen with other Elements, see HEAT (pp. 952-961).

On the quantities of Oxygen consumed in the Imperfect Combustion of Gases and Gaseous Mixtures, see CHEMICAL ACTION (pp. 430-436).

Occurrence in the Sun.—The presence of oxygen in the sun has been discovered by H. Draper (*Sill. Am. J.* [3], xiv. 89), by the appearance of *bright* lines in the solar spectrum coinciding with those of incandescent oxygen. The brightness of these lines is attributed by Draper to the very great thickness of the incandescent gas-stratum of the sun, which may reverse the effect of the phosphore. J. C. Draper, on the other hand (*ibid.* xvi. 256), has shown, by means of a diffraction-spectrum, that the solar spectrum contains numerous very fine dark lines coinciding with the bright lines of the oxygen spectrum and extending to the ultra-violet.

Preparation.—In preparing oxygen from potassium chlorate, it is advantageous, according to J. Löwe (*Dingl. pol. J.* cxxiii. 533), to mix the chlorate with about an equal weight of recently ignited ferric oxide (*Caput mortuum*) instead of cupric oxide or manganese dioxide. Previous fusion of the chlorate is also to be recommended.

On the preparation of Oxygen, see also S. Zinno (*Chem. News*, xxxvi. 168).

On the Evolution and Absorption of Oxygen by Plants, see PLANTS.

On the Relative Affinities of Oxygen and Sulphur for Metals, see SULPHUR.

Reaction with Sodium Hyposulphite and with Cuprous Oxide.—When a solution of sodium hyposulphite, Na_2SO_3 , is added to aerated water tinted with indigo, the indigo is decolorised when a quantity of the liquid has been added sufficient to consume just half the oxygen present. The liquid thus decolorised becomes blue again under the influence of the slightest trace of free oxygen, and the gases extracted from it by ebullition or by the mercurial pump consist of nitrogen and carbon dioxide without appreciable traces of oxygen.

If an excess of a colourless solution of ammoniacal cuprous chloride is added to aerated water, the liquid becomes blue, and on titrating by means of hyposulphite the cupric oxide which has been formed, its amount is found to be equivalent to half that of the dissolved oxygen. Certain reducing agents, notably sodium hyposulphite and ammoniacal cuprous chloride in presence of oxygen dissolved in water, divide the oxygen into two equal parts, one of which acts upon the reducing agent itself, the other remaining disguised in the liquid. The oxygen which thus disappears probably unites with the water, forming hydrogen peroxide. It becomes free again on heating the liquid. Stannite of sodium, however, removes the whole of the dissolved oxygen (Schützenberger a. Risler, *Compt. rend.* lxxvi. 1214).

Estimation.—On the estimation of Free Oxygen in Water and in Blood by means of the Hyposulphite reaction above described, see BLOOD (vii. 200); also *Chem. Soc. J.* 1873, 936. Remarks thereon by König a. Mutschler (*Ber.* x. 2017; *Jahresb. f. Chem.* 1877, 1035).

On the estimation of Oxygen in Water, see also Endemann (*Amer. Chem.* v. 9), and H. Wurtz (*ibid.* 10); also *Jahresb. f. Chem.* 1874, 963; further, *Amer. Chem.* v. 237, 364.

On the estimation of the total amount of Oxygen in Commercial Copper, see COPPER (p. 561).

On the direct estimation of Oxygen in Organic Compounds, see ORGANIC ANALYSIS (p. 1445).

OXYHÆMOGLOBIN. From recent experiments by Hoppe-Seyler (*Zeitschr. physiol. Chem.* i. 396), it appears that this substance, when treated in aqueous solution with palladium-hydrogen, in a vessel from which the air is excluded, is completely converted into methæmoglobin. This latter must therefore contain less oxygen than oxyhæmoglobin and cannot be a peroxyhæmoglobin, as supposed by Jäderholm (p. 920). Methæmoglobin is converted by putrefaction, in the absence of oxygen, into hæmoglobin, which by cautious treatment may be converted into oxyhæmoglobin, and more readily into carbonyl-hæmoglobin.

OXYHEPTIC ACID, $\text{C}_7\text{H}^{10}\text{O}_2$. See HEPTIC ACID (p. 1020).

OXYHEPTOIC ACID, $\text{C}_7\text{H}^{10}\text{O}_2$. See CENANTHYLIC ACID (p. 1427).

OXYISOBUTYRIC ACID. See OXYBUTYRIC ACIDS (p. 1468).

OXYISODINAPETHYL, See NAPHTHYL-COMPOUNDS.

OXYISOLEPIDIN, $C^{28}H^{20}O^2$. See LEPIDIN (p. 1177).

OXYISOPHTHALIC ACID. See OXYPHTHALIC ACID, under PHTHALIC ACIDS.

OXYISOKYLENE QUINONE. See XYLENE QUINONES.

OXYITACONIC ACID, $C^8H^5O^3 = HO.HC \equiv C \begin{smallmatrix} CO^2H. \\ CH^2CO^2H. \end{smallmatrix}$. An acid produced, together with formic acid, by the action of boiling baryta-water on aconic acid (vii. 22).

OXYKETONES. The introduction of an acid radicle into the hydroxyl-group of phenol gives rise to a body which is capable of reacting further with an acid chloride to form the ether of an oxyketone. Thus, for instance, the introduction of the benzoyl-radicle into phenol produces phenyl benzoate, and this substance reacts with benzoyl chloride and zinc chloride in such a manner as to form benzoyl-phenyl benzoate, $C^6H^5.CO.O.C^6H^4.CO(C^6H^5)$ (Doebner, *Ber.* x. 1968).

In like manner, the action of zinc chloride on a mixture of benzoyl chloride and resorcinol produces two benzoiorescinols, $C^6H^5.CO.C^6H^3(OH)^2$ and $(C^6H^5.CO)^2C^6H^2(OH)^2$, which, by the further action of benzoyl chloride, are converted into dibenzoates (Doebner a. Stackmann, *Ber.* xi. 2268). See RESORCINOL.

OXYLEPIDINS, $C^{28}H^{20}O^2$ and $C^{28}H^{20}O^3$. See LEPIDIN (pp. 1173, 1176).

OXYLEUCATIN. A constituent of Coto bark (p. 574).

OXYMALEIC ACID. Syn. with Hydroxymaleic acid, $C^4H^3(OH)O^3$. See MALEIC ACID (p. 1256).

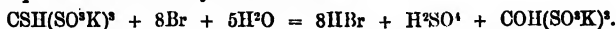
OXYMALONIC ACID. Syn. with Hydroxymalonic acid, $C^4H^3(OH)O^3$. See MALONIC ACID (p. 1260).

OXYMESITYLENIC ACID, $C^9H^{10}O^3$, appears to be formed, together with mesitol (p. 1282), by fusing potassium mesitylenesulphonate with potassium hydroxide (Biedermann a. Ledoux, *Ber.* viii. 57).

OXYMETHANESULPHONIC ACID, $CH^3SO^4 = CH^2(OH).SO^3H$. *Methyl-isethionic acid* (Max Müller, *Ber.* vi. 1031). This acid, metameric with methylsulphuric acid, $(CH^3)HSO^4$ or $SO^2(OCH^3)(OH)$, is obtained by distilling sulphuric anhydride (2 mol.) into a well-cooled mixture of methyl alcohol (1 mol.) with a large quantity of concentrated sulphuric acid. The resulting liquid is diluted with water, boiled for some hours and neutralised with lead carbonate, the lead is removed by hydrogen sulphide, and then filtered, and the filtrate neutralised with potassium carbonate. By repeated crystallisation, the pure *potassium salt* is obtained in large anhydrous orthorhombic crystals moderately soluble in water, insoluble in alcohol. The *barium salt* forms small limpid plates; the *ammonium salt*, small easily soluble needles. The free acid, as well as its salts, is very stable, not being decomposed by boiling with water or with concentrated acids.

Oxymethanedisulphonic acid, $CH(OH)(SO^3H)^2$, is formed by passing the vapour of sulphuric anhydride into pure methyl alcohol. The action is very violent, the liquid blackening and giving off sulphur dioxide, even when it is well cooled with a freezing mixture. When the liquid in the receiver is so far supersaturated with sulphuric anhydride as to give off thick fumes, it is to be treated in the manner above described for the preparation of oxymethanemonosulphonic acid. The product is a dark-coloured *potassium salt*, which may be freed from colouring matters by digestion with boiling alcohol of 40 per cent. and obtained by crystallisation from hot water in concentric groups of needles. The *barium salt* is produced by mixing a dilute solution (1 : 80) of the potassium salt with barium chloride, and separates after a while in small well-formed needles. Both the acid and its salts are as stable as the oxymethanemonosulphonates. The disulphonic acid may also be prepared by heating potassium oxymethanemonosulphonate for four or five hours with fuming sulphuric acid.

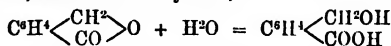
Oxymethanetrissulphonic acid, $C(OH)(SO^3H)^3$. *Methyl-alkoholtrissulfosäure* (Albrecht, *Liebig's Annalen*, clxi. 129). The potassium salt of this acid is obtained by dropping bromine into a warm solution of potassium methylmercaptan-trisulphonate till the liquid exhibits a faint yellowish colour:



The salt then separates in beautiful needles, which, after recrystallisation and drying, have the composition $COH(SO^3K)^3 + H^2O$. By slow crystallisation it is obtained in fine monoclinic strongly refracting prisms. It dissolves in 81 pts. of water at 21°. The *free acid*, obtained by precipitating the solution of the potassium salt with basic lead acetate, and decomposing the precipitate with hydrogen sulphide, dries up on

evaporation in a vacuum to a deliquescent crystalline mass. It does not give any colour-reaction with ferric chloride. The *ammonium salt*, $\text{COH}(\text{SO}^3\text{NH}^4)^2$, prepared by neutralisation, forms thin tabular anhydrous crystals immediately soluble in water. The *barium salt*, $[\text{COH}(\text{SO}^3)^2]^2\text{Ba}^2 + 8\text{H}_2\text{O}$, is precipitated by barium chloride from a hot aqueous solution of the potassium salt in nacreous laminae, dissolves in a very large quantity of water, and crystallises therefrom in small shining needles. The *copper salt* is less characteristic. A *basic mercuric salt*, $[\text{COH}(\text{SO}^3)^2]^2\text{Hg}^2 \cdot 3\text{HgO} + 15\text{H}_2\text{O}$, is obtained by dissolving moist mercuric oxide in the free acid. The *silver salt*, $\text{COH}(\text{SO}^3\text{Ag})^2 + \text{H}_2\text{O}$, crystallises in tufts of needles, easily soluble in warm water. A *plumbiferous potassium salt*, obtained by evaporating the liquid remaining over the precipitate formed on mixing a solution of potassium oxymethanetrissulphonate with normal lead acetate, was found to have the composition $4\text{COH}(\text{SO}^3\text{K})^2 + [\text{CO}(\text{SO}^3\text{K})^2]^2\text{Pb} + 6\text{H}_2\text{O}$. A double salt of lead oxymethanetrissulphonate with lead acetate, $[\text{COH}(\text{SO}^3)^2]^2\text{Pb}^2 + (\text{C}^2\text{H}^3\text{O}^2)^2\text{Pb} + 8\text{H}_2\text{O}$, is obtained in efflorescent tabular crystals when the precipitate formed on adding basic lead acetate to the solution of the potassium salt is dissolved in dilute acetic acid, and the solution is left to evaporate. It is decomposed by boiling water, with formation of lead sulphate.

OXYMETHYLBENZOIC ACID, $\text{C}^6\text{H}^4\text{O}^3 = \text{C}^6\text{H}^4(\text{CH}^2\text{OH})\text{COOH}$ (J. Hessert, *Ber.* x. 1445; xi. 237). This acid is formed by the action of alkalis or alkaline carbonates on phthalide, which is its anhydride,



It is much less soluble in cold water than phthalide, but dissolves easily in alcohol and ether. It melts at 118° , giving up 1 mol. water, and being reconverted into phthalide; the same change takes place also on boiling the acid with water. It is a well-defined monobasic acid, reddens litmus strongly, and dissolves with effervescence in alkaline carbonates. Its salts are all soluble in water; those of the alkaline earths dissolve in very small quantities of water and of alcohol, but are not deliquescent. The *silver salt*, $\text{C}^6\text{H}^4(\text{CH}^2\text{OH})(\text{COOAg})$, obtained by the action of the acid on recently precipitated silver oxide, crystallises from aqueous solution in small octohedrons. The *lead salt* is decomposed by water.

OXYMETHYLOXYBENZOIC ACIDS, $\text{C}^6\text{H}^4(\text{OH})(\text{CH}^2\text{OH})(\text{COOH})$. The modifications 1 : 2 : 4, 1 : 2 : 6, and 1 : 4 : 6 of these acids are obtained, as already described, by reduction of para-aldehydro-salieylic, ortho-aldehydro-salieylic, and ortho-aldehydro-para-oxybenzoic acids respectively (see ALDEHYDO-OXYBENZOIC ACIDS (p. 1465)).

OXYNAPHTHALENE, OXYNAPHTHOIC ACIDS, OXYNAPHTHOL, OXYNAPHTHAQUINONE. See NAPHTHALENE, &c.

OXYNEURINE, $\text{C}^6\text{H}^{11}\text{NO}^2$. Syn. with BETAINE (pp. 323, 880).

OXYPARACONIC ACID, $\text{C}^8\text{H}^6\text{O}^3$. The calcium salt of this acid is formed, together with calcium itatartarate, when a solution of chloritamalic acid neutralised with calcium carbonate is heated for some time to the boiling point. See CITRIC ACIDS (PYRO-), p. 518.

OXYPEUCEDANIN. See PEUCEDANIN.

OXYPHENYLACETIC ACID, $\text{C}^8\text{H}^7\text{O}^3 = \text{CH}^2(\text{OC}^6\text{H}^5)\text{COOH}$. *Phenyl-oxacetic* or *Phenyl-glycollic acid*.—This acid, which Heintz obtained as a sodium salt by heating sodium phenate with chloracetic acid (p. 918), is converted by heating with alcohol into an ethyl salt, $\text{CH}^2(\text{OC}^6\text{H}^5)\text{CO}^2\text{C}^2\text{H}^5$, which boils at 251° , and yields the corresponding amide when treated with aqueous ammonia. The calcium salt yields by dry distillation a liquid of high boiling point. Cold strong nitric acid converts oxyphenylacetic acid into the *dinitro-derivative*, $\text{C}^8\text{H}^3(\text{NO}^2)^2\text{O}.\text{CH}^2.\text{COOH}$. The *mononitro-derivative*, obtained by the action of sodium monochloracetate on sodium nitrophenol (prepared from volatile nitrophenol), melts at 153° , and volatilises easily with vapour of water (P. Fritzsche, *J. pr. Chem.* [2], xix. 33).

OXYPHENYLPHthalIMIDE

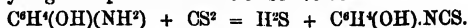
or

OXYPHthalANIL,

$\text{C}^6\text{H}^4 \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{N} = (\text{CO})^2 = \text{C}^6\text{H}^4 \end{array}$ is formed by heating 1 mol. orthamidophenol and 1 mol. phthalic anhydride for some time to about 220° , and may be purified by exhausting the solidified and pulverised mass with boiling alcohol, and recrystallising the crystals which separate on cooling, several times from boiling alcohol, with addition of animal charcoal. It is thus obtained in prisms having a faint yellow colour, melting at 220° , easily soluble in alcohol and in toluene, especially when heated; it dissolves also on heating with alkalis and alkaline carbonates, forming salts of oxyphthalanilic

acid, $C^6H^4(OH).NH.CO.C^6H^4.COOH$. The *sodium salt* of this acid, $C^{14}H^{10}NaO^4$, crystallises from water in fine needles. The acid itself, obtained by decomposing the salt with dilute hydrochloric acid, and recrystallising the resulting precipitate from alcohol, forms prisms melting at 223° . Corresponding derivatives of paramidophenol have not been obtained (Ladenburg, *Ber.* ix. 1524).

OXYPHENYLTHIOCARBIMIDE, $C^6H^4(OH).NCS$, is obtained by boiling an alcoholic solution of orthamidophenol with carbon disulphide in a stream of hydrogen, as long as hydrogen sulphide continues to be evolved :



The product freed from alcohol by slow evaporation deposits the thiocarbimide in yellowish-grey crystalline crusts, and on recrystallising these from alcohol and boiling water, it is obtained in broad nearly colourless needles melting at 196° . It does not volatilise with aqueous vapour, but carbonises when heated above its melting point. It dissolves readily in ammonia, and crystallises therefrom unaltered.

Silver nitrate added to the ammoniacal solution throws down white flocks which do not blacken on boiling. Oxyphenylthiocarbimide is decomposed by boiling *aniline* with formation of hydrogen sulphide, and by *hydrochloric acid* at 170° into carbon dioxide, hydrogen sulphide, and amidophenol (J. Dunner, *Ber.* ix. 465).

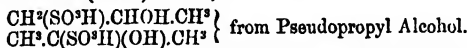
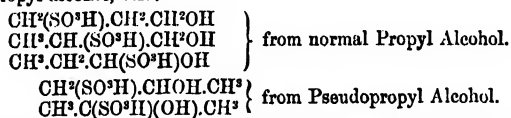
OXYPTHALIC ACID. See PHTHALIC ACIDS.

OXYPTHALYL-PARAMIDOBENZOIC ACID,

$C^6H^4 \begin{smallmatrix} CO.NH.C^6H^4.COOH \\ COOH \end{smallmatrix}$, formed by oxidation of paratolylphthalimide,

$C^6H^4(CH^3)-C^6H^4 \begin{smallmatrix} CO \\ CO \end{smallmatrix} NH$, with permanganate, is nearly insoluble in water, melts with decomposition at $275^\circ-277^\circ$, and is converted by heating with hydrochloric into paramidobenzoic acid (A. Michael, *Ber.* x. 576).

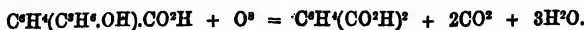
OXYPROPANE-SULPHONIC ACID, $C^3H^6(OH)(SO^3H)$ (Max Müller, *Ber.* vi. 1441). This acid admits of five modifications, three derived from normal and three from pseudopropyl alcohol, viz.:



Only one of these is however known, and is obtained by the three following processes: (1). By passing the vapour of sulphuric anhydride into normal propyl alcohol till the liquid begins to fume in the air, and treating the product in the manner already described for the preparation of oxymethanesulphonic acid (p. 1471). The salts of the acid thus obtained do not crystallise from aqueous solution, and they are so little soluble in hot absolute alcohol that only very small quantities can be crystallised therefrom; the potassium salt may however be readily crystallised in small needles by heating it with alcohol under pressure at about 140° . (2). By boiling allyl alcohol (b. p. 92°) with a concentrated solution of acid potassium sulphite, mixing the solution with a large excess of sulphuric acid, precipitating with alcohol (20 vols.), and treating the residue left on evaporating the alcoholic filtrate in the manner above mentioned: $C^3H^6O + SO^3H^2 = C^3H^6(OH)(SO^3H)$. (3). Acrolein, $CH^2=CH-CHO$, treated with excess of acid sodium sulphite, is converted into the oxydisulphonic acid, $CH^3.CH(SO^3H).CH(OH)(SO^3H)$ or $CH^3(SO^3H).CH^2-CH(OH)(SO^3H)$, which when decomposed yields sulphur dioxide, water, and an acroleinsulphonic acid, either $CH^3.CH(SO^3H).CHO$ or $CH^3(SO^3H).CH^2.CHO$, and this when heated with sodium-amalgam takes up 2 at. hydrogen, and is converted into oxypropane-sulphonic acid, $CH^3.CH(SO^3H).CH^2OH$ or $CH^3(SO^3H).CH^2.CH^2OH$.

OXYPROPYLBENZOIC ACID, $C^{10}H^{12}O^3 = C^6H^4(C^3H^6OH).COOH$ (R. Meyer, *Ber.* xi. 1283). This acid is formed, together with a small quantity of terephthalic acid, by oxidising cumic acid, $C^6H^4(C^3H^7).CO^2H$, dissolved in caustic soda with potassium permanganate. It is soluble in hot water, and separates from a strong aqueous solution in dendritic crystals, from a dilute solution in long thin prisms. It is very soluble in alcohol and ether, melts at $155^\circ-156^\circ$, and sublimes with partial decomposition. Its *ammonium salt* is soluble, and its neutral solution gives no reaction with ferric chloride. The *copper salt* is obtained first as a bright blue amorphous precipitate, which on standing becomes crystalline. The *lead salt* is obtained as a white amorphous precipitate, which melts in boiling water. The *silver salt*, $C^{10}H^{11}AgO^3$, is a white crystalline body, not easily acted on by light; and may be crystallised from hot water in beautiful, shining transparent, rhombic plates.

By oxidation with chromic acid mixture, oxypropylbenzoic acid is converted into terephthalic acid:



OXYPURPURIN. See PURPURIN.

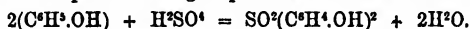
OXYPYROTARTARIC ACID. See PYROTARTARIC ACID.

OXYSALICYLIC ACID, $\text{C}^6\text{H}^3(\text{OH})^2(\text{CO}^2\text{H})^2$ [$\text{CO}^2\text{H} : \text{OH} : \text{OH} = 1 : 2 : 5$]. See p. 289. The so-called *gentisic acid*, obtained by Hlasiwetz a. Habermann from gentisin, the colouring matter of gentian root, by the action of melting potash, and at first supposed by them to be a dioxybenzoic acid different from the four previously known (p. 860), has been shown by subsequent experiments to be identical with oxy salicylic acid. *Pyrogentisic acid*, $\text{C}^6\text{H}^3\text{O}^2$, obtained by heating gentisic acid, and originally supposed to be a fourth modification of dihydroxybenzene, is now found to be identical with hydroquinone (Hlasiwetz a. Habermann, *Liebigs Annalen*, clxxx. 343).

OXYSUCCINYL-PARAMIDOBENZOIC ACID, $\text{C}^{11}\text{H}^{11}\text{NO}^5 = \text{C}^6\text{H}^4(\text{CO}^2\text{H})\text{NH}(\text{CO}^2\text{H})^2(\text{CO}^2\text{H})$, is formed by the action of potassium permanganate on paratolylsuccinimide, $\text{C}^6\text{H}^4(\text{CH}^2)\text{N}(\text{CO}^2\text{H})^2\text{CO}$, and crystallises in yellowish needles, melting at $225^\circ\text{--}226^\circ$, sparingly soluble in cold, freely in hot water, moderately soluble in cold, very easily in hot alcohol. When boiled with hydrochloric acid, it yields paramidobenzoic acid. The *ammonium salt* is moderately soluble; the *barium salt* is less soluble, and crystallises from hot water in laminae. The *lead salt* is a white, the *copper salt* a blue precipitate, both soluble in hot water. The *silver salt*, $\text{C}^{10}\text{H}^3\text{Ag}^2\text{NO}^5$, is a white flocculent precipitate. *Orthotolylsuccinimide* does not yield an acid by oxidation (A. Michael, *Ber.* x. 576).

OXYSULPHOBENZIDE, $\text{C}^{12}\text{H}^{10}\text{SO}^4 = (\text{C}^6\text{H}^4\text{OH})^2\text{SO}^2$. This compound, produced by the action of strong sulphuric acid on crystallised phenol, was discovered in 1867 by Glutz (vi. 894), and its methyl-, ethyl-, and amyl-derivatives, also its tetrachloro-derivative, were obtained in 1870 by Annaheim (vii. 886), who has since discovered and examined a large number of other derivatives (*Ber.* vi. 1206; viii. 1059; ix. 79; xi. 1668; *Liebigs Annalen*, clxxii. 28).

Preparation.—The best yield of oxysulphobenzide is obtained by heating two parts of pure phenol and one part of fuming sulphuric acid for 3–5 hours to $183^\circ\text{--}190^\circ$.



The product is purified by pouring the warm mass slowly into cold water and triturating it to convert it into a crystalline mass. The oxysulphobenzide thus obtained amounts to 63·5 per cent. of the weight of the phenol, and the mother-liquor contains only paraphenolsulphonic acid. If more sulphuric acid be used than is indicated by the above equation, much less oxysulphobenzide, or none at all, is obtained, because sulphuric acid readily acts on this compound at a high temperature. Thus when it is heated with an excess of common sulphuric acid for an hour or two to $180^\circ\text{--}190^\circ$, paraphenolsulphonic and disulphonic acids are produced, while by treating it at the same temperature with three times its weight of fuming sulphuric acid, a mixture of di- and trisulphonic acids is formed.

The crude oxysulphobenzide is purified by boiling it with water, which leaves a red oil; the crystals separating from the filtrate are again treated in the same way, and then recrystallised, first from a small quantity of boiling alcohol, then from water, whereby the compound is obtained in perfectly white glistening needles, melting at 293° .

Crystallisation.—To obtain measurable crystals, pure oxysulphobenzide is dissolved in a beaker nearly to saturation in glacial acetic acid at the boiling heat; the solution, without filtering, is immediately placed over a water-bath heated to 100° , a second beaker is inverted over it, and the whole is covered with a cloth and left for twenty-four hours. The crystals, 2 cm. long, thus obtained are orthorhombic, and exhibit the combination $\infty \bar{P} \infty \cdot \infty \bar{P}^2 \cdot 0P \cdot P$. Axes $a : b : c = 1.2829 : 1 : 0.53419$. Sp. gr. = 1.3663 at 15° , whence molecular volume = 182.9 (Annaheim).

Oxidation.—Oxysulphobenzide is completely oxidised by potassium permanganate, yielding the potassium salt, $(\text{C}^6\text{H}^4\text{OK})^2\text{SO}^2$, together with sulphate and oxalate. Potassium-oxysulphobenzide is soluble in alcohol, yielding an alkaline solution from which hydrochloric acid separates the oxysulphobenzide in a mass of shining crystals. If the quantity of permanganate used is insufficient to oxidise the whole of the oxysulphobenzide, part of the latter remains unattacked, and the rest is completely oxidised to sulphuric, oxalic, and carbonic acids, without formation of intermediate products (Guareschi, *Gazz. chim. ital.* 1878, 246).

Tetrachloroxysulphobenzide, $\text{SO}^2[\text{C}^6\text{H}^2\text{Cl}^2(\text{OH})]^2$, is produced, together with chloranil and other quinones, by adding to a mixture of 1 pt. of oxysulphobenzide and

2 pts. of potassium chlorate, 120–150 times its weight of hydrochloric acid. The product is washed with cold and warm water and cold alcohol, the residue dissolved in boiling alcohol, and an equal volume of boiling water added; on cooling, long white needles separate out, which are purified by recrystallisation. From strong alcohol the compound crystallises in large nacreous prisms melting at 288°–289°. It is insoluble in water, sparingly soluble in cold alcohol, freely in boiling alcohol, benzene, and ether. It combines with alkalis and decomposes carbonates.

Tetrabromoxysulphobenzide, $\text{SO}_2[\text{C}^6\text{H}^2\text{Br}^2(\text{OH})]^2$, may be obtained by the action of mercuric oxide and bromine on oxysulphobenzide in presence of water, but is best prepared by dissolving oxysulphobenzide in an excess of bromine and evaporating the solution on a water-bath. It crystallises from hot alcohol in short thick monoclinic prisms melting at 278°–279°, and dissolves readily in boiling amyl alcohol, in caustic alkalis and in alkaline carbonates, forming salts which do not crystallise.

Tetriodoxysulphobenzide, $\text{SO}_2[\text{C}^6\text{H}^2\text{I}^2(\text{OH})]^2$, is produced by dissolving 12.5 pts. of oxysulphobenzide and 51 of iodine in alcohol, and adding 30 of freshly prepared mercuric oxide. The product, after being washed with alcohol and ether, is boiled with water and potassium carbonate, and the solution is precipitated with hydrochloric acid. It is insoluble in water, cold alcohol, ether, benzene, carbon sulphide, and chloroform, almost insoluble in boiling alcohol and glacial acetic acid, separating from these solutions in microscopic needles melting at 260°–270°.

Methyloxysulphobenzide, $\text{SO}_2(\text{C}^6\text{H}^4\text{OCH}^3)^2$, is prepared by boiling an alcoholic solution of oxysulphobenzide, potash, and methyl iodide. It is insoluble in water and caustic alkalis, sparingly soluble in cold, and freely in boiling alcohol, crystallising on quick cooling, in thin square plates, and on slow evaporation in flat prisms, melting at 130°, and subliming when more strongly heated. On dissolving it in hot sulphuric acid, it yields a mono- and a di-sulphonic acid. The barium salt of the latter forms colourless, transparent, monoclinic crystals, resembling felspar, and consisting of $\text{C}^6\text{H}^3(\text{OCH}^3)(\text{SO}_3)^2\text{Ba} + 4\text{H}_2\text{O}$. The calcium salt contains also 4 mols. water, and crystallises in long, white glistening needles. Methyloxysulphobenzide is identical with Cahours' *sulphaniside*, obtained by the action of sulphuric acid on anisol.

Dibromomethyloxysulphobenzide, $\text{SO}_2(\text{C}^6\text{H}^3\text{BrOCH}^3)^2$, is obtained by adding the required quantity of bromine to the methyl-compound. It is insoluble in water and alkalis, sparingly soluble in cold, and readily in boiling alcohol, crystallising in beautifully white, small plates, which melt at 166°.

Dinitromethyloxysulphobenzide, $\text{SO}_2[\text{C}^6\text{H}^3(\text{NO}_2)\text{OCH}^3]^2$, is readily formed by dissolving the dry methyl-ether in fuming nitric acid. It is insoluble in water, cold alcohol, ether, and benzene, almost insoluble in boiling alcohol, and sparingly soluble in boiling glacial acetic acid, from which it crystallises in microscopic prisms melting at 214°–215°. By the action of phosphorus iodide and water, it is reduced to the corresponding diamido-compound.

Ethyloxysulphobenzide, $\text{SO}_2(\text{C}^6\text{H}^4\text{OC}^2\text{H}^5)^2$, dissolves readily only in ether and boiling alcohol, and crystallises in glistening small quadratic plates, melting at 159°.

Dibromethyloxysulphobenzide, $\text{SO}_2[\text{C}^6\text{H}^3\text{BrOC}^2\text{H}^5]^2$, resembles the corresponding methyl-compound, and forms plates melting at 183°.

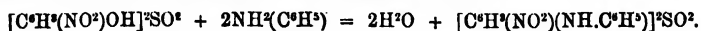
Dinitroethyloxysulphobenzide, $\text{SO}_2[\text{C}^6\text{H}^3(\text{NO}_2)\text{OC}^2\text{H}^5]^2$, crystallises from alcohol in large shining plates, or fine needles, melting at 192°. By reducing it with phosphorus iodide and water, *diamidoethyloxysulphobenzide hydriodide*, $\text{SO}_2[\text{C}^6\text{H}^3(\text{NH}_2)\text{OC}^2\text{H}^5]^2 + 2\text{HI}$, is formed, crystallising from water or alcohol in yellowish needles. From its solution alkalis precipitate the base as a crystalline powder.

Amyloxysulphobenzide, $\text{SO}_2(\text{C}^6\text{H}^4\text{OC}^3\text{H}^{11})^2$, requires a rather high temperature for its formation, and crystallises from boiling alcohol in small, brilliant, white plates, melting at 98°. Its *bromine-derivative*, $\text{SO}_2(\text{C}^6\text{H}^3\text{BrOC}^3\text{H}^{11})^2$, crystallises from hot alcohol in small white plates, melting at 100°. The *nitro-derivative*, $\text{SO}_2[\text{C}^6\text{H}^3(\text{NO}_2)\text{OC}^3\text{H}^{11}]^2$, is sparingly soluble in boiling alcohol, and forms brilliant, nacreous, six-sided plates or prisms, melting at 150°–151°. It differs from the other nitro-derivatives of oxysulphobenzide, in not being reduced by water and phosphorus iodide, or by tin and hydrochloric acid (Annaheim, *Liebig's Annalen*, clxxii. 38–59).

Dinitroxysulphobenzide, $[\text{C}^6\text{H}^3(\text{NO}_2)\text{OH}]^2\text{SO}_2$, separates from a solution of oxysulphobenzide in warm nitric acid, in crystalline scales; it is insoluble in water, only slightly soluble in alcohol, ether, and benzene, and crystallises from alcohol in microscopic rhombic needles. With alkalis and alkaline earths it forms easily soluble compounds having a deep yellow-red colour. The *barium salt*, $[\text{C}^6\text{H}^3(\text{NO}_2)\text{O}]^2\text{Ba} \cdot \text{SO}_2$, is prepared by dissolving dinitroxysulphobenzide in hot baryta-water, and separates from the solution—freed from excess of barium by carbonic

acid and evaporated—in crystalline crusts. The *sodium salt*, $[C^6H^4(NO^2)ONa]^+SO_3^-$, prepared in like manner, forms red-yellow crystalline crusts, and its aqueous solution gives precipitates, apparently of analogous composition, with silver, zinc, copper, and lead salts (Glutz, *loc. cit.*)

Dinitroxysulphobenzidanilide, $[C^6H^4(NO^2)(NH.C^6H^5)]^+SO_3^-$, is formed by heating the dinitro-compound just described with 2 pts. of aniline:



It crystallises from aniline in brilliant red rhombic prisms, exhibiting the combination $\infty P. 0P$. On boiling it with water, alcohol, ether, or benzene, it is decomposed with reproduction of aniline (Annaheim, *Ber.* vii. 436).

Diamidoxysulphobenzide, $C^{12}H^{12}N^2SO_4 = [C^6H^3(NH^2)OH]^+SO_3^-$. The *hydriodide* of this base, $C^{12}H^{12}N^2SO_4.2HI + 2H^2O$, is formed by the action of phosphorus iodide on dinitroxysulphobenzide in presence of a small quantity of hot water, and separates from the solution, after removal of the phosphorus, in long colourless needles which give off their water at 110° – 115° , and dissolve readily in water and in alcohol (Glutz, *Liebig's Annalen*, cxlvii. 52; Annaheim, *Ber.* vii. 436).*

The corresponding *hydrochloride*, $[C^6H^3(NH^2)OH]^+SO_3^- . 2HCl + 2H^2O$, obtained by reduction of the dinitro-compound with tin and hydrochloric acid, is a very similar body. The *sulphate*, $[C^6H^3(NH^2)OH]^+SO_3^- . H^2SO_4 + 2H^2O$, obtained by heating the hydrochloride with sulphuric acid, is slightly soluble in water and in alcohol, and crystallises from hot water in short thick prisms; it is very stable, and may be heated to 140° without decomposition. Ammonia added to the solution of this salt throws down the free base, which separates from water in large crystals.

On treating the sulphate or hydrochloride in acid aqueous solution with potassium nitrite, the liquid turns red and deposits a substance having a splendid vermilion colour, dissolving in ammonia with deep red colour, reprecipitated by acids, detonating when heated (Annaheim).

Tetranitro-oxyulphobenzide, $[C^6H^2(NO^2)_2OH]^+SO_3^-$, obtained by the action of red fuming nitric acid on the dry dinitro-derivative, and purified by crystallisation from hot water, is a solid straw-yellow, very bitter substance, melting at 253° , and exploding at a higher temperature. It is insoluble in most of the usual solvents, but crystallises in long needles from boiling water, the mother-liquor when mixed with hydrochloric acid yielding an additional crop. It has well-marked acid properties, and readily decomposes alkaline carbonates. It is extremely soluble in glacial acetic acid at the boiling heat, and separates almost completely on cooling in needles, in which, however, part of the remaining hydrogen is replaced by acetyl. Its *potassium salt*, $[C^6H^2(NO^2)_2OK]^+SO_3^-$, is sparingly soluble in cold, moderately soluble in hot water, and separates therefrom on cooling in reddish-yellow microscopic crystals, which detonate when heated. The corresponding *sodium salt* dissolves easily in water either hot or cold, and separates after a long time in minute yellow crystals. Another sodium salt, whose composition was not determined, was once obtained in hydrated efflorescent octohedral crystals 1 cm. long (Annaheim, *Ber.* xi. 1668).

Dibromodinitro-oxyulphobenzide, $[C^6H^2Br(NO^2)OH]^+SO_3^-$, is prepared by mixing 34 grams of dinitroxysulphobenzide (to which a little bisulphide of carbon has been added) with 32 grams of bromine, evaporating to dryness on the water-bath, washing with water, dissolving in sodium carbonate, and crystallising out the sodium salt.

Sodium dibromodinitroxysulphobenzide crystallises in small, yellowish-red needles, soluble in hot water, but with some difficulty in cold water. The free acid is separated from the solution on addition of hydrochloric acid. Dibromodinitroxysulphobenzide is insoluble in water, sparingly soluble in alcohol, but easily soluble in boiling acetic acid, from which it separates again in white needles of a faint straw colour. It melts at 284° – 285° .

Di-iododinitroxysulphobenzide, $[C^6H^2I(NO^2)OH]^+SO_3^-$, is prepared by bringing together 50 grams of iodine dissolved in alcohol, and a mixture of 34 grams of dinitroxysulphobenzide with 21.6 grams of yellow mercuric oxide, and heating on the water-bath. After filtration and washing with water, the product is boiled with sodium carbonate and extracted two or three times with boiling water. The difficultly soluble sodium salt separates from the hot solution in fine orange-red needles.

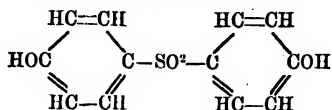
Di-iododinitroxysulphobenzide is insoluble in water and alcohol, but dissolves in boiling acetic acid. It melts at 294° – 296° . Like the previous compounds, it possesses acid properties and decomposes alkaline carbonates (Annaheim, *Ber.* ix. 660).

Tetraoxysulphobenzide, $[C^6H^2N=N.OH]^+SO_3^-$, is prepared by dissolving

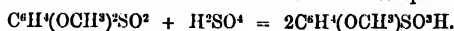
* Glutz assigned to this compound the formula $C^{12}H^{12}N^2SO_4.2HI = C^6H^4(NH^2)^2SO_4.2HI$; but the formula above given is more in accordance with its mode of formation, and is moreover supported by Annaheim's analysis.

15 pts. of the hydrochloride of diamidoxysulphobenzide in 70 pts. of alcohol, and adding 15 pts. of amyl nitrite. It forms six-sided microscopic laminae, which, when exposed to air and sunlight, are converted into a red colouring matter. It is insoluble in alcohol, but dissolves in water acidulated with hydrochloric acid; detonates violently at 120° (Annaheim, *Ber.* viii. 1059).

Constitution of Oxysulphobenzide.—Annaheim represents this substance by the formula



regarding it as formed of two benzene-nuclei directly united by the group SO^2 , and having the two hydroxyls in the para-positions with regard to that group. This view is supported: 1. By the reaction of oxysulphobenzide with sulphuric acid, whereby it is resolved into two paraphenol-monosulphonic acids, $\text{C}^6\text{H}_4\text{OH.H.H.SO}^3\text{H.H}^2$. 2. By the fact that the two hydroxylic hydrogen-atoms may be simultaneously replaced by alcohol radicles, and that the resulting compounds, e.g. sulphanisöilide, may in like manner be resolved into two molecules of one and the same compound,



3. By the fact that, as Annaheim has shown by heating oxysulphide with ethylene bromide, the two hydroxylic hydrogens cannot be replaced by the diatomic radicle ethylene, as might be expected if the two hydroxyls occupied contiguous positions (*Liebig's Annalen*, clxxii. 59).

OXYTHIOCARBAMIC ACID, $\text{NH}^2\text{CO.SH}$. See CARBAMIC ACID (p. 387).

OXYTHYMOQUINONE. See THYMOQUINONE.

OXYTOLUIC ACIDS. See TOLUIC ACIDS.

OXYTOLUIDINE. Syn. with AMIDOCRESOL. See TOLUIDINES.

OXYTRIMESIC ACID, $\text{C}^6\text{H}^2(\text{OH})(\text{COOH})^3$. This is the modification of phenol-tricarboxylic acid in which the three carboxyls are symmetrically disposed. See PHENOL-TRICARBOXYLIC ACID.

OXYUVITIC ACID, $\text{C}^6\text{H}^4\text{O}^3 = \text{C}^6\text{H}^2(\text{CH}^3)(\text{OH})(\text{CO}^2\text{H})^2$. This acid is formed on adding chloroform to the crude product of the action of sodium on ethyl acetate, and boiling the resulting mixture of ethers till a sample of it no longer yields an oily product with acids. On adding hydrochloric acid to the solution thus obtained, oxyuvitic acid separates in yellowish flocks; and on dissolving these in a large quantity of boiling water, and decolorising with animal charcoal, the acid is obtained in thin colourless needles. On the mode of its formation, see ACETO-ACETIC ETHERS (p. 17).

Oxyuvitic acid is but sparingly soluble in cold water, but dissolves more readily in hot water, still more in alcohol and ether. With ferric chloride it gives a red-violet, with ferrous salts a reddish coloration. It softens at 290°, and decomposes at the same time, so that its melting point cannot be determined.

The oxyuvitates of the alkali-metals are very soluble, crystallise indistinctly, and turn brown on exposure to the air. The *potassium salt* has the composition $\text{C}^6\text{H}^4\text{K}^2\text{O}^3 + \text{H}^2\text{O}$. The *barium salt*, $\text{C}^6\text{H}^4\text{BaO}^5 + 1\frac{1}{2}\text{H}^2\text{O}$, crystallises in microscopic needles, which easily turn yellowish: it is soluble in alcohol, gives off 1 mol. water at 125°, the rest at 150°. By distillation with lime, it yields a cresol boiling at 200°. The *calcium salt* has the composition $\text{C}^6\text{H}^4\text{CaO}^3 + 1\frac{1}{2}\text{H}^2\text{O}$. The *silver salt*, $\text{C}^6\text{H}^4\text{Ag}^2\text{O}^3$, separates, after long standing, as a curdy precipitate not quite insoluble in water; so likewise does the greenish *copper salt*, $\text{C}^6\text{H}^4\text{CuO}^3$. The solution of the barium salt gives with lead nitrate a white amorphous precipitate, with ferric chloride a brown-violet precipitate; none with mercuric chloride or zinc chloride (Oppenheim a. Pfaff, *Ber.* vii. 929).

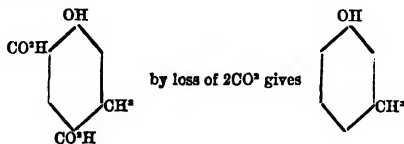
The *methyl ether*, $\text{C}^6\text{H}^2(\text{OH})(\text{CH}^3)(\text{COOCH}^3)^2$, produced by heating the silver salt at 100° with methyl iodide and perfectly anhydrous ether, forms yellow trapeziform plates several mm. long, melts at 108°, and sublimes between 200° and 300°.

Reactions.—1. By oxidation of oxyuvitic acid Emmerling a. Oppenheim (*Ber.* ix. 726) have obtained, not, as was expected, oxytrimesic acid, but an acid, $\text{C}^7\text{H}^4\text{O}^3$, isomeric with Böttinger's uvic acid, which they designate as *hydro-oxybenzoic acid* (see UVIC ACID). With chromic acid only a small product is obtained; with potassium permanganate a somewhat larger quantity, about 10 per cent. of the oxyuvitic acid employed.

2. *Fuming nitric acid*, either alone or mixed with sulphuric acid, converts oxyuvitic acid into a trinitrocresol, $C^6H^3(NO^2)^3O$, which after purification forms fan-shaped groups of faintly-yellowish smooth needles melting at 106° (Emmerling a. Oppenheim, *Ber.* ix. 1094).

3. Oxyuvitic acid treated with *phosphorus pentachloride* is converted into a mixture of chlorides, which when boiled with water yields, together with reproduced oxyuvitic acid, an acid which separates from the sufficiently concentrated mother-liquor in long needles, and appears from the analysis of its barium salt to be an anhydride of oxyuvitic acid, $[C^6H^2(OH)(CH^3)(COOH)CO]^2O$ (Oppenheim a. Pfaff, *Ber.* viii. 884).

Constitution.—Oppenheim a. Pfaff find that the cresol obtained by dry distillation of the calcium and barium salts of oxyuvitic acid is *metacresol*, a result which confirms the relative position of the radicles OH and CH^3 in the acid, as represented by the formula given on p. 17.



Hence also it follows that the acid here designated as oxyuvitic acid is not the true oxy- or hydroxy-acid of uvitic acid, which, according to Böttger, has the substituted radicles in the symmetrical position 1, 3, 5, or $C^6.CO^2H.H.CH^3.H.CO^2H.H$ (see *UVITIC ACID*).

OXYXYLENE, or **HYDROXYXYLENE**, $C^6H^3(CH^3)^2OH$. This is the constitution of *phlorol* (*q.v.*)

OXYXYLIC ACID, $C^6H^2(CH^3)^2(OH)(COOH)$. An acid formed by the action of melting potash on *pseudocumenol*, $C^6H^2(CH^3)^2OH$ (*q.v.*)

OZONE. On the formation of Ozone by the action of the silent electric discharge on oxygen, see *ELECTRICITY* (p. 727), also Giannetti a. Volta (*Ber.* ix. 84). A powerful apparatus for this purpose is described by Leeds (*Chem. News*, xl. 196). According to J. Bohe (*Ber.* vi. 439), the electrification of dry oxygen is the only method that yields pure ozone, all other methods giving rise at the same time to the formation of nitrous vapours or of hydrogen dioxide.

According to Böttger (*N. Rep. Pharm.* xxiii. 372), ozone is produced in the formation as well as in the electrolysis of water. When acidulated water is decomposed by an electric current, the ozone formed at the positive pole destroyed by addition of a small quantity of potash, and the mixed gases then exploded by contact with a flame, iodised starch-paper introduced into the cylinder which contained them is turned blue.

Experiments on the formation of ozone by combustion in the air have been made by W. Radulocitsch (*Ber.* vii. 1454). When wax, stearin, petroleum or magnesium was burnt within a bottomless flask, and the products of combustion were made to pass through a glass tube containing strips of iodised starch paper, the formation of ozone was shown by the bluing of the paper; when however the same substances were burnt in ordinary lamps, the formation of ozone could not be detected. When a small quantity of petroleum (boiling at 30° to 100° and upwards, and of sp. gr. 0.67 to 0.68 at 22°) is placed in a capacious flask which is frequently opened and shaken, it acquires oxidising properties, and the air contained in the flask gives the ozone reaction. This occurs in a few days at the summer temperature if the vessel is exposed to the direct rays of the sun, and more slowly at a lower temperature and in diffused daylight. The slow evaporation appears to play an important part. When petroleum thus treated is shaken up with a solution of potassium iodide, iodine is liberated, and paper prepared with potassium iodide and starch-paste acquires a blue colour when exposed to the air in the flask. The altered petroleum also decolorises indigo, gives a blue colour to guaiacum extract, and exhibits the other reactions of active oxygen. When the petroleum is shaken up with water, the latter remains neutral, and when tested shows the presence of hydrogen peroxide; but, if the petroleum has remained for a long time in contact with the air, it acquires an acid reaction which it communicates to water when agitated therewith. The aqueous solution is found still to contain hydrogen peroxide, but it also reduces silver nitrate, thus indicating the presence of formic acid. Petroleum readily absorbs ozone—liberated from potassium permanganate by the action of sulphuric acid—and when agitated with water gives to it an acid reaction, whilst the solution reduces silver salts; but the petroleum is not at once capable of liberating

iodine from potassium iodide solution. If however allowed to stand for twenty-four hours, it acquires that property, and if it be then agitated with water, the solution gives the characteristic reactions of hydrogen peroxide.

Similarly, pure benzene, and the portion of light coal-oil boiling between 80° and 100°, exhibit the same power of rendering oxygen active. Pure phenol mixed with water also acquires, in contact with air, the power of turning paper blue which has been prepared with potassium iodide and starch-paste (Fadakowski, *Ber.* vi. 106). Similar observations have been made by E. Schæfer (*ibid.* 406).

An apparatus constructed by O. Loew for the preparation of ozone for industrial purposes, depending on the ozonisation of oxygen by the combustion of coal-gas or other hydrogenised bodies in a rapid stream of air, is described by Ad. Ott (*Dingl. pol. J.* cxxiii. 130). The use of such an apparatus is suggested for the defusolation of brandy, or the manufacture of vinegar.

On the supposed formation of Ozone by the oxidation of Turpentine-oil and other essential oils, see Kingzett (p. 1430).

On the ozonisation of Air by moist Phosphorus, see A. R. Leeds (*Chem. News*, xl. 70; *Chem. Soc. J.* xxxvi. 881).

Bellucci (*Ber.* viii. 905; ix. 581) observed in the neighbourhood of the water-falls of Terni and Trollhättan a strong smell of ozone, which he attributes to the friction of the particles of water in the spray, and the consequent development of electricity. He finds that the spray of water containing solid substances in solution generates more ozone than that of pure water, and that the effect is still further increased if the water holds solid particles in suspension.

From experiments by Bellucci (*Ber.* vi. 756; *Compt. rend.* lxxviii. 362) it appears that the oxygen exhaled from plants in sunlight does not exhibit the properties of ozone.

Amount of Ozone in Air.—The following average results for the several months of the year 1873, obtained with Lender's ozonometer, are recorded by A. v. Löseke (*Arch. Pharm.* [3], v. 427):

	Ozone-degree	Temperature	Amount of rain
January . . .	9.35	— 0.40°	
February . . .	9.90	— 2.00	
March . . .	9.30	+ 2.30	
April . . .	8.76	+ 4.30	
May . . .	8.45	+ 6.50	
June . . .	8.66	+ 11.90	7.06 cm.
July . . .	8.30	+ 14.00	5.98
August . . .	8.32	+ 12.70	4.57
September . . .	7.86	+ 8.50	6.95
October . . .	8.55	+ 6.47	5.56
November . . .	2.26	+ 1.45	5.59
December . . .	5.60	— 1.70	1.43

The mean for the winter half-year was 8.4, for the summer half-year 7.5, and for the day-time 7.94. The proportion of ozone in a yard surrounded by moderately high buildings was about 2° lower; in dwelling-rooms and other apartments, whether the windows were closed or opened for a longer or shorter time, and whether growing plants were placed in the room or not, no ozone could be detected; neither was any connection observed between the amount of ozone and the direction of the wind (compare Houzeau, vii. 113, 114).

According to L. Fautrat (*Compt. rend.* lxxxiii. 752), the proportion of ozone in the air of forests is smaller than in the open country.

Experiments on the gradual conversion of ozone into ordinary oxygen have been made by Berthelot (*Compt. rend.* lxxxvi. 76) by means of flasks of about 260 c.c. capacity filled with oxygen ozonised by the discharge and kept at a temperature of about 12°. At the commencement of the experiment, the gas contained 2.2 per cent. of ozone; in twenty-four hours the amount was reduced to 2.1 per cent.; in five days to 1.5 per cent.; in fourteen days to 0.4 per cent.; after fifty-one days only a trace remained, and in sixty days no ozone could be detected either by the smell or by potassium iodide. Ozone has no fixed tension of dissociation, and the rate of destruction is directly proportional to the amount contained in the mixture. The dissociation did not appear to be accelerated by the presence of water, at least in the first week.

Relations of Ozone to Water.—The solubility of ozone in water, first observed by Williamson in 1845 (*Liebig's Annalen*, liv. 130), is corroborated by the experiments of Carius (*ibid.* clxiv. 1) and of Schöne (*Ber.* vi. 1208, 1224). Rammelsberg, how-

ever (*ibid.* vi. 603), observes that diluted ozone is not absorbed by water at ordinary temperatures, the absorption taking place only when the gaseous mixture contains a considerable proportion of ozone. Carius, on the other hand, finds that water in contact with its own bulk of a gas containing 2 per cent. of ozone, acquires its odour and characteristic properties. Even when the gas contains only 1 per cent. of ozone, the solution produces a powerful effect on potassium iodide and starch, but diminution of the proportion of ozone leads very rapidly to an extreme weakening of the solution. Ozone, mixed with oxygen gas, obeys in fact the law of gaseous absorption which makes the quantity dissolved proportional to that fraction only of the total pressure which is due to the quantity of the gas itself contained in the mixture. Taking this law into account, Carius found, from a series of closely agreeing experiments, that the mean absorption-coefficient of water for ozone at 1° and 760 mm. pressure is 0.834. As, however, it is by no means certain that the limit of absorption was attained in these experiments, the actual absorption-coefficient may be even greater than that deduced from observation.

The following results have been obtained by Schöne (*Ber.* vi. 1208, 1224).

(1). Ozone does not oxidise water into peroxide of hydrogen. (2). Ozone is absorbed by water in considerable quantity even at the ordinary temperature. The observed maximum was 0.189 gram, or 8.31 c.c. (reduced) ozone (O³) per litre. (3). Ozone in contact with water suffers no qualitative alteration. (4). The quantity of ozone in ozonised oxygen is diminished by passing the gas through water. By collecting dry ozonised oxygen over water, about one-fourth of the ozone is removed, and the loss of ozone is greater after prolonged contact. (5). Since in the passage of ozonised oxygen through water, far more ozone disappears than is absorbed by the water during the time, and as the loss of ozone continues even when the water is saturated with it, it would seem that water has in this case the power of breaking up ozone. (6). Ozonised oxygen, left at rest in contact with water at the ordinary temperature for some days, becomes changed into ordinary oxygen. (7). The change of ozone into ordinary oxygen in the above manner is accompanied by an increase in volume. This result accords with that obtained by heat in the researches of Andrews a. Tait, and by Soret. Schöne likewise observes that ozone may remain for some time in contact with the skin without suffering decomposition.

From the numbers obtained by Carius, Schöne calculates for the absorption-coefficient of ozone at 16.5° the number 0.373, agreeing nearly with that deduced from his own experiments, viz. 0.366.

According to Carius (*loc. cit.*), the dissociation of ozone by water at 0° is very small. The aqueous solution, even when extremely dilute, exhibits the characteristic taste and smell of ozone, the smell even in a solution containing only 5 vol. ozone in 100 vol. water being so powerful that it can never be mistaken for that of a solution of nitrous acid, chlorine, chlorous acid, or hypochlorous acid. Delicate litmus-paper is quickly bleached by concentrated ozone-water, but in a more dilute solution the bleaching is preceded by a peculiar shade of colour resembling indistinct reddening by an acid. Concentrated ozone-water exhibits all the oxidising effects of gaseous ozone. A solution of thallous oxide produces, slowly in dilute, quickly in concentrated ozone-water, a brown precipitate of thallic oxide. The formation of silver peroxide, on the other hand, does not take place with certainty even in the most concentrated ozone-water, but only when silver leaf is introduced into the small space above the solution in a closed vessel where it can come in contact with the gases emitted from the liquid. Ozone-water prepared with ozonised air contains abundance of nitric acid, but no nitrous acid or hydrogen dioxide (Carius).

Decolorising Power.—Goppelsroeder (*Dingl. pol. J.* cexix. 540) publishes an observation made by Koechlin, according to which pieces of calcic which had been dyed with indigo treated with sulphuric acid, then washed, and frozen by exposure in the moist state to a winter atmosphere, were found to be considerably altered in colour, especially on the edges. This effect is attributed by Goppelsroeder, on the ground of special experiments, to the action of atmospheric ozone. In the same manner aniline-brown on cotton was changed to a yellow-orange; fuchsine-rosa, Hofmann's blue and violet, red corallin, iodine-green, lakes from dye-woods, and even Turkey-red, were completely bleached. In the absence of water, however, this action of ozone did not take place.

Antiseptic Power.—Boillot (*Compt. rend.* lxxxi. 1258) recommends the use of ozone for the preservation of meat, milk, and other easily alterable articles of food.

Action on Blood.—According to Doziel (*N. Rep. Pharm.* xxiv. 431) the action of ozone on blood is exerted in the first instance on the red corpuscles, their colouring matter being separated, and the blood in a quarter of an hour acquiring a darker colour. Defibrinated blood, exposed in thin layers to the prolonged action of ozone,

acquires the colour of red sealing-wax, and the blood, after this alteration, no longer deposits crystals of hæmoglobin on addition of alcohol, ether, or chloroform. Defibrinated blood through which ozone was passed for a considerable time deposited flocks which, after washing with water, were indistinguishable from fibrin; by the still further prolonged action of ozone, the blood became dingy green and finally colourless. The formation of the fibrinoid substance is probably due to an alteration of hæmoglobin. Hæmatin is likewise decolorised by ozone. When blood poisoned with carbon monoxide is exposed to the action of ozone, it quickly acquires the properties of normal blood, carbon dioxide being separated at the same time. Blood containing carbon monoxide is less quickly decolorised by ozone than normal blood, and does not so quickly lose the property of depositing crystals of hæmoglobin. The alteration of the blood-corpuscles by ozone must not be confounded with that produced by carbon dioxide.

Estimation.—To estimate ozone in presence of chlorine and nitrogen tetroxide, D. Tommasi (*Chem. News*, xxix. 284) passes the gaseous mixture in the first instance immediately through a normal solution of potassium ferrocyanide, and secondly through a tube filled with platinum black or manganese dioxide to destroy the ozone, and then through the normal solution of potassium ferrocyanide.

M. Davy (*Compt. rend.* lxxxii. 157) estimates the very small amount of ozone present in the air, which varies from 0.76 to 1.3 mg. in 100 c.c. of air, by passing the air through a solution of neutral potassium arsenite and a little potassium iodide, and determining the amount of arsenious acid thereby oxidised, by means of a standard iodine-solution.

P.

PALLADIUM. Small quantities of this metal are of almost constant occurrence in refined silver; that of Commern and Mechernich on the Eifel contains 0.0053 per cent. palladium (H. Rössler, *Liebig's Annalen*, clxxx. 240). Palladium is also found, together with other platinum metals, in the ferric chloride obtained in the preparation of fine gold (Opificius, *Dingl. pol. J.* cxxiv. 414; *Jahresh. f. Chem.* 1877, 1142).

Electromotive Force in Gas-batteries.—According to E. Villari (*Pogg. Ann.* cli. 608), the electromotive force of palladium in gas-batteries is considerably greater than that of platinum electrodes, evidently in consequence of the great affinity of palladium for hydrogen; moreover, it becomes considerably greater when the (positive) electrode in contact with the oxygen is oxidised.

On the use of Palladium in facilitating oxidation, see HYDROCARBONS (p. 1065).

Coquillion (*Compt. rend.* lxxxiii. 394) recommends the use of palladium instead of platinum wire for igniting mixtures of hydrocarbons and air in gas-analysis, inasmuch as it brings about the combination of the gases without detonation.

On the Absorption of Hydrogen by Palladium and the properties of Palladium-hydrogen, see HYDROGEN (pp. 1070, 1071).

When palladium in the form of sponge or foil is heated in a flame of alcohol or coal-gas, it becomes coated with a thick spongy layer of soot, and on burning this away, the palladium remains in the form of a brittle skeleton.

Spongy palladium, which at 100° is capable of taking up several hundred times its own volume of hydrogen gas, does not act on ethylene at any temperature below a red heat; but on raising the heat to redness, carbon is deposited and hydrogen set free, the temperature at which this decomposition takes place being below that at which ethylene is decomposed by heat without the agency of palladium. The effect appears to be due to the absorption of hydrogen and its subsequent separation, these phenomena continually succeeding one another in the same manner as when copper is ignited in ammonia-gas (Wöhler, *Liebig's Annalen*, clxxiv. 128).

Palladium may be *amalgamated* in the same way as iron (p. 1096), viz. by bringing it in contact with sodium- or ammonium-amalgam, and then dipping it into acidulated water.

The *black oxide of palladium*, PdO, obtained by ignition of the nitrate, is instantly reduced by hydrogen, even at ordinary temperatures, the reaction being attended with vivid incandescence. In like manner, as observed by Berzelius, palladium which has acquired a blue tarnish by oxidation immediately loses its blue colour when plunged into hydrogen gas at the ordinary temperature (Wöhler, *Liebig's Annalen*, clxxiv. 60).

On *Palladium Mercaptide*, see MERCAPTIDES (p. 1276).

A soluble *palladium thiocyanate* is obtained, according to S. Kern (*Chem. News*, xxxii. 242), by mixing the aqueous solution of palladium chloride or nitrate and potassium thiocyanate. The solution of this salt is said to give no reaction with an alcoholic solution of iodine.

Palladammonium compounds.—Yellow palladammonium chloride, $\text{PdCl}^2 \cdot 2\text{NH}^3$ or $\text{Pd}(\text{NH}^3\text{Cl})^2$, treated with aqua regia, is converted into the compound $\text{Pd}^2\text{Cl}^6 \cdot 4\text{NH}^3$ or $\text{ClPd}(\text{NH}^3\text{Cl})^2$, which is a dark red, almost black substance, closely resembling in appearance and solubility the double chloride of iridium and ammonium. Its formation may be represented by the equation $2(\text{PdCl}^2 \cdot 2\text{NH}^3) + \text{Cl}^2 = \text{Pd}^2\text{Cl}^6 \cdot 4\text{NH}^3$. The same salt was obtained as a precipitate on treating some mother-liquors of dipalladammonium chloride, $\text{PdCl}^4 \cdot 4\text{NH}^3$, with aqua regia in presence of sal-ammoniac. It is interesting as showing that all the metals of the platinum group, except platinum itself, are capable of forming chlorides of the formula M^2Cl^6 . It is easily decomposed by heat, breaking up into hydrochloric acid, sal-ammoniac, nitrogen, and metallic palladium. It is also decomposed by boiling water, with brisk evolution of nitrogen, the palladium trichloride being reduced to dichloride, a portion of which remains in combination with the undecomposed ammonia (Deville & Debray, *Compt. rend.* lxxvii. 926).

PALMITONE, $\text{CO}(\text{C}^{15}\text{H}^{31})^2$. See KETONES (p. 1149).

PANCREATIC FERMENTS (p. 779). E. Schoffer (*Pharm. J. Trans.* [3], vi. 844) prepares pancreatin as follows: The freshly chopped pancreas of an ox is macerated for twenty-four hours with water slightly acidulated with hydrochloric acid; the acid liquid is poured off and replaced by pure water, which again is poured off after four to six hours, and mixed with the acid extract; the filtered liquid is neutralised with recently precipitated calcium carbonate, then filtered again; and this second filtrate is mixed with an equal volume of alcohol, whereby the pancreatin is thrown down in white flocks, which dissolve almost completely in water, convert starch into sugar, and decompose neutral fats, with separation of the free acids. Pancreatin is decomposed by *pepsin* dissolved in acidulated water.

v. Mering & Musculus (*Zeitschr. physiol. Chem.* i. 395), by treating starch and glycogen with pancreatic and salivary ferment, have obtained dextrin and maltose; also dextrose with pancreatic ferment.

On the action of the Organised Ferments of the Pancreas on *Carbohydrates* and *Nitrogenous Bodies*, see FERMENTS (p. 782).

By the pancreatic digestion of gelatin, Nencki (*Ber.* vii. 1593) obtained a very small quantity of indole and small quantities of tyrosine, ammonia, leucine, glycocine, and a viscid yellow body, which he calls *gelatin-peptone*.

PANDERMITE. A mineral found at Panderna, on the Black Sea, in a grey streaky gypsum bed, lying under a formation composed of alternating layers of brown clay and calcareous slate. It occurs in snow-white, fine-grained nodules and fragments enclosed in the gypsum. An analysis of the dried mineral showed it to have the following composition:

CaO	MgO	FeO	K ² O	H ² O	B ² O ³
29.33	0.15	0.30	0.18	15.45	54.59 = 100.00

which may be represented by the formula $2\text{CaO} \cdot 3\text{B}^2\text{O}^3 + 3\text{H}^2\text{O}$, indicating that pandermite is nearly related to borocalcite. No chlorine, sulphuric acid, silica, or carbonic acid, could be detected in it (G. vom Rath, *Jahrb. f. Min.* 1878, 74).

PAO. See PEREIRO.

PAPER. On the Chemical Manufacture of Paper from Wood, see Rosenhain (*Dingl. pol. J.* ccxx. 81; *Chem. Soc. J.* xxx. 234; also *Chem. Soc. J.* xxv. 1048; xxvi. 1069).

Manufacture of Paper from the Gombo (*Hibiscus esculentus*), see p. 896 of this volume.

Micrographical Study of the Manufacture of Paper: A. Gerard (*Compt. rend.* lxxx. 629; *Chem. Soc. J.* xxviii. 675).

Parchment-paper: *Dingl.* ccxx. 380; *Jahresb. f. Chem.* 1876, 1174.

Japanese Paper: Munroe (*Amer. Chem.* vi. 409; *Jahresb.* 1876, 1175).

Dendritic Spots on Paper: Liversidge (*Chem. Soc. J.* xxv. 646); Hadrian (*ibid.* xxvii. 754).

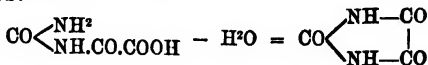
On the Glazing of Paper: C. Wurster (*Dingl.* ccxxvi. 75, 310, 381; *Chem. Soc. J.* xxxiv. 184).

On the Estimation of Mineral Matter in Paper: Wurster (*Dingl. ccxxvii.* 179; *Chem. Soc. J.* xxxiv. 528).

Estimation of Colouring Matter in Paper: Wurster (*Dingl. ccxxviii.* 168; *Chem. Soc. J.* xxxiv. 823).

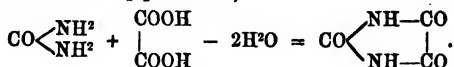
PARABANIC ACID, $C^3H^2N^2O^3 = CO \begin{matrix} \text{NH}-CO \\ | \\ \text{NH}-CO \end{matrix}$ Oxalyl-carbamide, or

Oxalyl-urea.—This compound is produced: 1. By the action of phosphorus oxychloride on oxaluric acid:

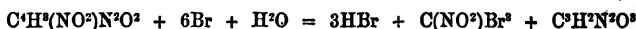


Well-dried oxaluric acid is heated to 200° in an oil-bath with three times its weight of phosphorus oxychloride as long as hydrogen chloride is given off; the residual white mass is dissolved in water; the solution filtered and evaporated to dryness; the residue pressed and dissolved in boiling alcohol; the alcoholic solution filtered and evaporated to dryness; and the oxalyl-carbamide thus obtained is purified by twice recrystallising it from boiling water (Grimaux, *Compt. rend.* lxxvii. 1548).

2. By the action of phosphorus trichloride on a mixture of oxalic acid and urea (Ponomareff, *Bull. Soc. Chim.* [2], xviii. 97):



3. By oxidising pyvuril, $C^3H^4N^4O^3$ —the diureide of pyruvic acid—with nitric acid, the pyvuril being first converted into mononitropyvuril-monoureide, $C^4H^3(NO^2)N^2O^3$, which, when distilled with 2 or 3 pts. bromine and 25 to 30 water, is resolved into bromopierin and parabanic acid:



(Grimaux, *Compt. rend.* lxxix. 1478).

Parabanic acid separates from aqueous or alcoholic solution in shining laminae having a sour taste; it may be heated to 200° without alteration, but at higher temperatures it yields a white sublimate, gives off pungent vapours smelling of cyanic acid, and leaves a carbonaceous mass. Its solution is not clouded by calcium acetate, but when boiled with potash it gives off ammonia, and if then supersaturated with acetic acid, it gives a copious precipitate with calcium salts.

A hydrate of parabanic acid, $C^3N^2H^2O^3.H_2O$, is obtained by subjecting 1 pt. uric acid to the action of 3 pts. nitric acid of sp. gr. 1.3 at about 60° , and keeping the temperature towards the end of the process between 35° and 55° according to the energy of the reaction. On subsequently heating the solution to 70° , the hydrate separates in large crystals (Tollens a. Wagner, *Liebig's Annalen*, clxvi. 321; Tollens, *ibid.* clxxv. 227). The same hydrate was obtained by Ponomareff (*Bull. Soc. Chim.* [2], xviii. 97) by the action of phosphorus trichloride on a mixture of urea and oxalic acid. The action begins at ordinary temperatures and is accompanied by rise of temperature and evolution of hydrochloric acid, and on cooling, the hydrate is obtained as a crystalline mass which dissolves easily in water and crystallises in thin colourless prisms.

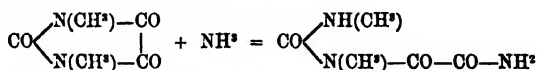
This hydrate is very stable, sustaining only a very slight decrease of weight when heated to 100° ; between 150° and 160° , however, the water is slowly driven off. The reddish aqueous solution of the residual dry mass no longer yields large crystals of the hydrate, but the well-known broad needles of the anhydrous compound. The hydrate dissolves in water more readily than the anhydrous compound, and is thereby distinguished from oxaluric acid, with which it is isomeric (Tollens a. Wagner).

Salts. The *diargentic salt* of parabanic acid, obtained by precipitation, was described by Liebig a. Wöhler (iv. 339). The *mono-argentic salt* and the *alkali-salts* have been obtained by Menshutkin (*Liebig's Annalen*, clxxii. 73). On account of the ready convertibility of parabanic into oxaluric acid, the preparation of these salts succeeds only under peculiar conditions. The *ammonium salt* is obtained as a white bulky crystalline precipitate on adding alcoholic ammonia to a solution of parabanic acid in absolute alcohol. Gaseous ammonia is but slowly absorbed by parabanic acid. The salt is very easily decomposable, and in aqueous solution is converted, even at ordinary temperatures, and more quickly during evaporation by heat, into ammonium oxalurate. When heated for six or eight hours to 100° in a sealed tube with alcoholic ammonia (absolute alcohol saturated at ordinary temperature with ammonia gas), it is converted into oxaluramide. The same result is obtained by merely

heating parabanic acid with alcoholic ammonia, just as aniline parabanate is converted into phenyl-oxaluramide (iv. 339). The *potassium salt* is obtained as a light white precipitate on adding rather less than the theoretical quantity of *potassium ethylate* (solution of potassium in absolute alcohol) to a solution of parabanic acid in absolute alcohol. The presence of water (or potassium hydrate) gives rise to the formation of oxalurate; excess of potassium ethylate produces oxalate. Potassium parabanate is insoluble in alcohol; water converts it into oxalurate. The *sodium salt* is prepared like the potassium salt, and exhibits similar properties. The *diargentic salt* is obtained as a crystalline precipitate having the composition $C^8N^2Ag^2O^3 + H^2O$, on adding silver nitrate to a solution of parabanic acid or of ammonium parabanate. [Liebig & Wöhler obtained it anhydrous by precipitating the aqueous acid with silver nitrate; Strecker obtained it as a hemihydrate, $2C^8N^2Ag^2O^3 + H^2O$, on mixing the aqueous acid with silver nitrate and a little ammonia (iv. 339).] The *mono-argentic salt*, $C^8N^2HAgO^3$, is obtained as a crystalline precipitate on adding silver nitrate (1 mol.) to a recently prepared solution of potassium parabanate, treating the resulting precipitate, after washing, with a quantity of nitric acid not sufficient to dissolve the whole of it, and mixing the warm solution with ammonia; also by mixing the aqueous solutions of 2 mols. parabanic acid with 3 mols. silver nitrate, removing the diargentic salt formed at the same time by filtration, precipitating the warm mother-liquor with ammonia, and purifying the precipitate as above. The salt thus produced is sometimes anhydrous, sometimes contains 1 mol. H^2O ; in the latter case it is isomorphous with silver oxalurate, from which, however, it differs by being less soluble in water, and by being converted into the diargentic salt when its solution in nitric acid is mixed with silver nitrate and ammonia (Menschutkin).

Methyl-parabanic Acid, $C^8N^2H(CH^3)O^3$, is best prepared by heating methyl-uric acid with 5 or 6 pts. of nitric acid, sp. gr. 1.30, till the liquid is no longer coloured by ammonia. The excess of acid is driven off by heat, and the residue diluted with a little water is exhausted with ether, which on evaporation leaves the methyl-parabanic acid as a residue which soon crystallises in translucent prisms, to be purified by pressure and recrystallisation. The same compound is formed by the prolonged action of boiling nitric acid on methyl-alloxan (H. Hill, *Ber.* ix. 370).

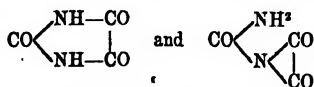
Dimethyl-parabanic Acid, $C^8N^2(CH^3)^2O^3 = CO \begin{matrix} \diagup N(CH^3)-CO \\ \diagdown N(CH^3)-CO \end{matrix}$ (also called *choleostrophane*, i. 926; iv. 340), is produced by heating the dry silver salt to 100° with methyl iodide, also by the action of chlorine or nitric acid upon caffeine. It crystallises from hot alcohol in prisms melting at 155.5° ; it also sublimes and distils at 275° – 277° , apparently without decomposition. Alcoholic ammonia converts it into dimethyloxaluramide, which melts with decomposition at 225° , and dissolves but sparingly in alcohol even at the boiling heat:



Dimethyl-parabanic acid is not attacked by acids, but is completely decomposed by alkalis (Menschutkin, *Liebig's Annalen*, clxxviii. 201).

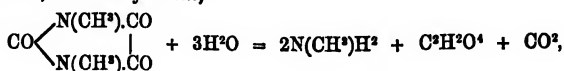
Constitution of Parabanic acid.—The conversion of parabanic acid into oxaluric acid by assumption of water, and its synthesis from oxalic acid and urea (p. 1483), prove beyond doubt that it is an anhydride intermediate in composition between the two last-named substances, or, in other words, an anhydride of oxaluric acid,

$CO \begin{matrix} \diagup NH^2-CO.OH \\ \diagdown NH-CO \end{matrix}$. These considerations however do not suffice for the complete establishment of its constitution; for oxaluric may lose a molecule of water in several different ways, leading to as many different constitutional formulæ, of which two at least may be regarded as equally well entitled to represent the constitution of parabanic acid, viz.



The first of these, which is the usually accepted formula of the acid, differs from all the rest in having its two hydrogen-atoms symmetrically attached to the two nitrogen-atoms, and its correctness may be tested by an examination of the products of decomposition of dimethyl-parabanic acid under the influence of acids. For, if each of the

two methyl-groups in this compound is attached to a nitrogen-atom as above represented, it must be resolved by assumption of the elements of water into oxalic acid, carbon dioxide, and methylamine,



whereas the unsymmetrical formula, $\text{CO} \begin{array}{c} \text{N(CH}_3\text{)}^2 \\ | \\ \text{N(C}^2\text{O}^2\text{)} \end{array}$, would require the formation of a mixture of ammonia and dimethylamine, and all the other possible formulæ would imply the formation either of pure ammonia or of a mixture of ammonia and methylamine. Now it has been shown by A. Calm (*Ber.* xii. 624) that dimethyl-parabanic acid heated to 200° with hydrochloric acid is actually resolved into CO², oxalic acid and pure methylamine: hence the first of the two formulæ above given for parabanic acid may be regarded as established.

PARABUXINE. See BUXINE (p. 365).

PARACAMPHORIC ACID. See MESOCAMPHORIC ACID (p. 1286).

PARACONIC ACID, C⁸H⁶O⁴. This acid, isomeric with citraconic, itaconic, and mesaconic acids, is formed by abstraction of HCl from itamono-chloropyrotartaric acid (vi. 760), and may be regarded as an anhydride of itamalic acid, C⁸H⁸O³:



(Swarts, *Bull. Acad. royal Belgique* [2], xxxiii. No. 1 [1872]; *Jahresb. f. Chem.* 1873, 585).

PARACOTOÏN. A constituent of Coto-bark (p. 573).

PARACRYLIC ACID. See DIACRYLIC ACID (p. 46).

PARACYANOCARBONIC ACID. See CYANOCARBONIC COMPOUNDS, POLYMERIC (p. 618).

PARA-DERIVATIVES, AROMATIC. *Paraldehydosalicylic acid.* See BENZOIC ACIDS, ALDEHYDO-OXY- (p. 288).

Parabenzoyl-benzoic acid. See p. 310.

Parabenzoyl-benzyl Chloride, Parabenzoyl-benzylene Dichloride and *Parabenzoyl-benzenyl Trichloride.* See TOLYL-PHENYL KETONES (p. 1155).

Parabenzoyl-toluene, C⁶CH³.H.H.C⁷H³O.H², obtained by distilling a mixture of calcium paratoluene and benzoate, and fractionating the product, is a slightly coloured fragrant oil, boiling at 310°–312°, and gradually crystallising when left at rest. By oxidation with chromic acid it is converted into parabenzoyl-benzoic acid (Radziszewski, *Ber.* vi. 810).

Parabromacetanilide, C⁸.NH(C²H³O).H.H.Br.H², prepared by treating parabromaniline with excess of acetyl chloride, washing the product with water, and recrystallising from alcohol, forms large, many-faced prisms, sometimes perfectly transparent and colourless with a vitreous lustre, sometimes opaque and white with nacreous lustre. It is moderately soluble in alcohol, nearly insoluble in cold water, slightly in hot water. Melts at 165.4° (Körner, *Gazz. chim. ital.* 1874, 329).

Parabromaniline, C⁶.NH².H.H.Br.H². See BENZENES (BROMAMIDO-), p. 193. This base is resolved by distillation into [1 : 2 : 4] dibromaniline, melting at 79.5°, and tribromaniline, C⁶.NH².Br.H.Br.H.Br, melting at 117° (E. Büchner, *Ber.* viii. 361).

Parabromobenzyl Compounds. *Parabromobenzyl alcohol*, C⁶H⁴.Br.CH²OH, is most easily prepared by boiling parabromobenzyl bromide with water for some days, in a flask with reversed condenser. It is also obtained by heating parabromobenzyl acetate to 150°, with aqueous ammonia. It forms long, colourless, elastic, flat needles, having a fine nacreous lustre and unpleasant odour, melting at 69°, and dissolving easily in boiling water, alcohol, ether, benzene, and carbon disulphide.

The *acetate*, formed by heating the bromide with sodium acetate in alcohol, decomposes when distilled, and has not yet been obtained pure.

The *cyanide*, C⁶H⁴.Br.CH²CN, is obtained by boiling the bromide with alcoholic solution of potassium cyanide. It is a crystalline body of strong disagreeable odour,

melting at 46° , and dissolving easily in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, but not in water.

The *thiocyanate*, $C^6H^4Br.CH^2SCN$, formed by boiling the bromide with potassium thiocyanate, crystallises in needles, melting at 25° , and dissolving very easily in alcohol.

Parabromalphatoluic acid, $C^6H^4Br.CH^2.COOH$, formed by heating the above cyanide to 100° , with hydrochloric acid in sealed tubes, crystallises in long white needles, which melt at 114.5° . It decomposes carbonates very slowly, but dissolves readily in ammonia and soda-ley, forming salts. By oxidation with chromic acid it is converted into parabromobenzoic acid. The ammonium salt forms precipitates with mercuric, mercurous, ferrous and lead salts, but not with salts of aluminium, chromium, zinc, cobalt, nickel, or magnesium.

Parabromobenzyl bromide reacts with ammonia at ordinary temperatures, forming triparabromobenzylamine, $(C^6H^4Br.CH^2)^3N$, and the corresponding hydrobromide, $(C^6H^4Br.CH^2)^3N.HBr$. The base crystallises from alcohol in needles melting at $78-79^{\circ}$; the hydrobromide is deposited from the alcoholic liquid in which it is formed, in white nacreous scales melting at 270° , insoluble in water and in alcohol, but easily soluble in ether (Jackson a. Lowery, *Ber.* ix. 1209).

Parabromometabromobenzoic acid, $C^6.CO^2H.H.Br.Br.H^2$. See BENZOIC ACIDS, DIBROMO- (p. 261).

Parabromorthonitraniline, $C^6.NH^2.NO^2.H.Br.H^2$. See BENZENES, NITROBROMAMIDO- (p. 200).

Parabromoparanitrodiphenyl, $C^{12}H^8Br(NO^2)$, m. p. 173° ; b. p. above 360° . See DIPHENYL (p. 661).

Parabutynylanisole, $C^{11}H^{14}O = C^6H^4(OCH^3).CH=CH.CH^2.CH^3$. This appears to be the compound formed, with separation of CO^2 , by heating methyl-paraoxyphenylangelic acid, $C^{12}H^{14}O^3$ (Perkin, p. 505).

Parachloracetanilide, $C^6.NH(C^2H^3O).H.H.Cl.H^2$, obtained by the action of acetyl chloride on parachloraniline, crystallises from acetic acid in long needles melting at 172.5° . Treated with a mixture of nitric and sulphuric acids, it yields a nitro-derivative convertible by sodium carbonate into parachlororthonitraniline, $C^6.NH^2.NO^2.H.Cl.H^2$ (p. 202), (Beilstein a. Kurbatow, *Ber.* vii. 1760).

Parachloramidotoluene. See TOLUIDINES.

Parachlorobenzamide and *Anilide*. See BENZOIC ACIDS, CHLORO- (p. 262).

Paracyananiline, $C^6.NH^2.H.H.CN.H^2$, is formed by heating para-uramido-benzoic acid: $C^6H^4N^2O^3 = C^7H^4N^2 + CO^2 + H^2O$, and crystallises in small white shining prisms melting at 86° (Griess, *Ber.* viii. 860).

Paradiphenyl-benzene. See DIPHENYL-BENZENE (p. 665).

Paradiphenyl-carboxylic acid or *Paraphenyl-benzoic acid*, $C^6.CO^2H.H.H.C^6H^3.H^2$ (p. 667).

Paradinitrophenyl-nitranilines, $NH(C^6H^4NO^2)[C^6H^3(NO^2)^2]$. See BENZENES, NITROBROMAMIDO- (p. 199).

Parabromosalicylic acid and *Aldehyde*. See TOLUIC (HYDROXY-) ACID and ALDEHYDE.

Parahydrazoxydiidobenzene. See PARAZOXYDIIDOBENZENE (p. 1487).

Para-iodacetanilide, $C^6.NH(C^2H^3O).H.H.I.H^2$, is formed as a dark crystalline precipitate by heating acetanilide with 1 mol. iodine chloride. It dissolves easily in hot water, and crystallises therefrom in white rhombic plates; dissolves also in alcohol and in glacial acetic acid; melts at 181.5° . On boiling it with hydrochloric acid and treating the resulting salt with ammonia, para-iodaniline melting at 60° is obtained.

Para-iodacetanilide is decomposed by strong nitric acid, with separation of iodine; but when its solution in glacial acetic acid is treated with nitric acid, para-iodonitranilide, $C^6H^3(NO^2)(NH^2)$, is formed, which crystallises from alcohol in orange-yellow needles melting at 122° , slightly soluble in water, more freely in alcohol and glacial acetic acid. It does not unite with hydrochloric acid (Michael a. Norton, *Ber.* xi. 107).

Para-iodobenzyl Compounds (Mabery a. Jackson, *Ber.* xi. 55-58).—*Para-iodobenzyl bromide*, $C^6H^4.I.CH^2Br = C^6.CH^2Br.H.H.I.H^2$, formed by the action of bromine on para-iodotoluene at temperatures above 116° , crystallises in white flat needles, having an aromatic odour, and melting at 78.75° . It sublimes in needles, and dissolves in hot alcohol, ether, benzene, and carbon bisulphide, but not in water.

Para-iodobenzyl alcohol, $C^6H^4.I.CH^2OH$, produced by boiling the bromide with

water, forms white silky scales of unpleasant odour, melting at 71·75°, and dissolving easily in alcohol, ether, benzene, and carbon bisulphide; sparingly in water.

Para-iodobenzyl cyanide, $C^6H^4I.CH^2ON$, crystallises from alcoholic solution in white pearly laminæ, which melt at 50·5°, and resemble the preceding compounds in solubility.

Para-iodoalphanolonic acid, $C^6H^4I.CH^2.COOH$, obtained by heating the nitril at 100° with fuming hydrochloric acid, forms white pointed plates, of agreeable odour, melting at 135°, and subliming at a somewhat higher temperature. By oxidation with chromic acid it is converted into para-iodobenzoic acid. Its *silver salt* crystallises from solution in boiling water in brilliant plates, easily soluble in dilute nitric acid. The *barium* and *calcium salts* form easily soluble white needles. The *zinc* and *magnesium salts* are crystalline, and sparingly soluble. Precipitates are produced by an ammoniacal solution of the acid in solutions of cupric sulphate, lead acetate, mercurous nitrate, aluminic and ferric chlorides, and nickel nitrate.

Para-iodobenzylamines.—The bromide, when heated with alcoholic ammonia, yields a bulky precipitate, which is resolved by crystallisation into the two following bodies:—

1. *Tri-para-iodobenzylamine*, $(C^6H^4I.CH^2)^3N$, the less soluble product, crystallises in white needles, melting at 114·5°, and dissolving easily in ether, benzene, and carbon bisulphide. It forms with platinic chlorido yellow needles of the salt, $[(C^6H^4I.CH^2)^3NH]^2PtCl^6$.

2. *Di-para-iodobenzylamine*, $(C^6H^4I.CH^2)^2NH$, the more soluble product, forms white needles, melting at 76°. It forms with hydrochloric acid a salt, crystallising in thick white plates, of very high melting-point, easily soluble in carbon bisulphide and glacial acetic acid. The platinochloride, $[(C^6H^4I.CH^2)^2NH]^2PtCl^6$, forms pale-yellow crystals.

Para-iodobenzyl thiocyanate, $C^6H^4I.CH^2.SCN$, formed by the action of the bromide on potassium thiocyanate, crystallises in long white plates of pleasant odour, melting at 40°. It dissolves easily in ether, benzene, carbon bisulphide, and glacial acetic acid; sparingly in alcohol.

Paraldehydosalicylic acid, $C^6.CO^2H.OH.H.H.CO.H$. See BENZOIC ACIDS (ALDEHYDO-OXY), p. 288.

Paralyl-anisoil, or *Anethol*, $C^6.OCH^3.H.H.C^3H^3.H^2$, is formed, with evolution of CO^2 , by the action of heat on methylparaoxyphenylcrotonic acid, $C^6.OCH^3.H.H.C^3H^3(CO^2H).H^2$ (Perkin, p. 505).

Para-nitraniline, $C^6.NH^2.H.H.NO^2.H^2$. See BENZENES (NITRAMIDO-), p. 198.

Paraoxybenzoic acid and *Aldehyde* (pp. 285, 304, 1459, 1465).

Paraoxybenzyl Alcohol, $C^6.OH.H.H.CH^2OH.H^2$. See OXYBENZYL ALCOHOLS (p. 1468).

Parapicrylnitranilines and *Parapicrylmetapicrylamine*. See BENZENES (NITRAMIDO-), p. 199.

Parasulphamine-benzoic or *Parasulphobenzamic acid*, $C^6H^4(SO^2NH^2)COOH$. See BENZOIC ACIDS (SULPHO-), p. 294.

Parasulphobenzin. See PHENYL SULPHIDE.

Parasulphobenzicarboxylic acid, $C^6H^4(SO^2)(C^6H^4)(CO^2H)$. See SULPHONES.

Parasulphobenzoic acid, $C^6.CO^2H.H.H.SO^2H.H^2$. See BENZOIC ACIDS (SULPHO-), p. 293.

Parathiobenzoate, *Tolylic*, $C^6H^4O.S.C^3H^3$. See THIOBENZOIC ACID.

Paratolyl. See TOLYL.

Paravinyl-anisoil, $C^6H^4(OCH^3)(C^2H^3)$, is produced, with evolution of CO^2 , by the action of heat on methylparaoxyphenylacrylic acid (p. 504).

Para-xylene. See XYLENE.

Paraoxydiiodobenzene, $C^{12}H^4I^2ON^2 = \begin{matrix} C^6H^4I-N \\ | \\ C^6H^4I-N \end{matrix} > O$, is formed by heating

10 pts. pariodonitrobenzene, m. p. 171°–172° (vi. 269), with 16 pts. potassium hydroxide and 100 pts. alcohol. It crystallises in light yellow plates and scales, melts at 199° to 199·5°, is insoluble in cold alcohol, slightly soluble in hot alcohol, also in glacial acetic acid and in ether, easily in benzene, nitrobenzene, and carbon sulphide. Heated for an hour to 100° in a sealed tube with alcoholic ammonium sulphide,

it is converted into parahydrazodiiodobenzene, $\begin{matrix} C^6H^4-NH \\ | \\ C^6H^4I-NH \end{matrix}$, which crystallises

in white or slightly yellow laminæ or flat needles, easily soluble in alcohol, glacial acetic acid, benzene, and nitrobenzene; melts at a temperature above 100° . By boiling with hydrochloric acid it is decomposed, with separation of iodine. Its alcoholic solution, treated with ferric chloride or boiled with animal charcoal, yields parazodi-

iodobenzene, $\begin{array}{c} \text{C}^6\text{H}^4\text{I}-\text{N} \\ || \\ \text{C}^6\text{H}^4\text{I}-\text{N} \end{array}$, which crystallises in reddish scales, slightly soluble in

alcohol and glacial acetic acid, easily in hot benzene, nitrobenzene, and carbon sulphide, melts at 237° , and volatilises at higher temperatures, leaving a trace of charcoal. The same compound is obtained by dissolving parazoxydiiodobenzene in strong sulphuric acid, and separates on cooling in brown needles having a steel-blue lustre, while immersed in the liquid (Gabriel, *Ber.* ix. 1405). On the corresponding meta-compounds, see p. 1287.

PARADIGITOGENIN. One of the numerous substances obtainable, according to Schmiedeberg (*Pharm. J. Trans.* [3], v. 741), from *Digitalis*.

PARADIPIC ACID, $\text{C}^8\text{H}^{10}\text{O}^4$, and **PARADIPIMALIC ACID**, $\text{C}^8\text{H}^{10}\text{O}^3$. See ACRYLIC ACID (pp. 46, 47).

PARAFFINS, $\text{C}^n\text{H}^{2n+2}$. On Paraffins from Petroleum, see PETROLEUM.

The several paraffins, Methane, Ethane, Propane, Butane, Pentane, Hexane, and Octane, are described in their alphabetical places.

On heptane, C^7H^{16} , from Pennsylvanian petroleum and the alcohols derived from it, see p. 1024.

Heptane from *Pinus sabiniana*. This tree, which is indigenous in California, and is known locally as the *Nut Pine* or *Digger Pine*, yields, when incisions are made in its bark, a terebinthinate from which, by distillation, an oily hydrocarbon is obtained, known in San Francisco as an article of commerce under the names of abietene, erasine, aurantine, theoline, &c., and used as a substitute for benzolin or petroleum-benzene for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless, mobile liquid having a strong aromatic odour, recalling that of orange-oil, and differs greatly in most of its physical properties from the terpenes obtained from most coniferous trees, boiling, after rectification, at 101° , and having a sp. gr. of 0.694 at 16.5° , whereas oil of turpentine boils at 160° , and has a sp. gr. of 0.840 at about the same temperature (W. Wenzell, *Pharm. J. Trans.* March 30, 1872).

This hydrocarbon has been further and very carefully examined by T. E. Thorpe (*Chem. Soc. J.* xxxv. 296), who has shown that it consists of normal heptane, $\text{CH}^3(\text{CH}^2)^4\text{CH}^3$. It affords the first instance of a paraffin playing the part of turpentine-oil in the vegetable kingdom, the only natural sources of heptane hitherto known being petroleum, and some of the fossil-fish oils obtained from Groenland, Switzerland, and other places.

The crude oil when distilled began to boil a little below 100° , the greater part distilling below 101° . The residual portion darkened slightly, and left on evaporation a small quantity of brown resinoid matter having in a very high degree the peculiar smell of the oil, indicating that the odour of the crude oil might be due in great part to the resin in solution; and this proved to be the case, for on agitating the oil with strong sulphuric acid, the acid became brown, and the liquid when again distilled was found to have lost the smell of orange oil.

The pure oil boils at 98.42° under a pressure of 760 mm. Its sp. gr. in the state of vapour is by experiment 49.94; by calculation 50.07 ($H=1$); in the liquid state 0.70057 at 0° . Its rate of expansion by heat is represented by the formula:

$$1 + 0.00121023 t + 0.00000111331 t^2 + 0.00000001174 t^3,$$

where t is the temperature reckoned from 0° .

The volume at 0° being 1, that at the boiling point is 1.14111: hence the sp. gr. at this temperature is 0.61393, which gives for heptane the specific volume 162.54. Kopp's values ($C=11$; $H=5.5$) gave the number 165.

The refractive index of the heptane for the line D, determined by the method of minimum deviation is 1.3879. Its specific refractive energy, $\frac{\mu-1}{d}$, where d is the density of the liquid at 17.6° , is 0.565; whence the molecular refractive energy is 56.4, a value agreeing closely with the computed number 55.8 deduced from Landolt's data, $C=5$, $H=1.3$.

The heptane is slightly active to polarised light, producing in a column 200 mm. long a deviation of $6^{\circ} 9'$.

On the viscosity and surface-tension of the liquid, see the original paper (pp. 302-308).

A comparison of the sp. gr. and boiling point of the heptane from *Pinus sabiniana*, with those of normal heptane from petroleum and of heptane obtained by heating azelaic acid with caustic baryta, yields the following results:

	Normal Heptane from Petroleum	Heptane from Azelaic acid	Heptane from <i>P. Sabiniana</i>
Boiling point . . .	98°-98.6°	98°-99°	98.42°
	(bar. 750.3 mm.)		
Sp. gr. at 0° . . .	0.7301	0.7000	0.70057

With the exception of the higher sp. gr. of the petroleum heptane, which is at present unaccountable, these values point to the conclusion that the heptanes from these three sources are identical.

Solid Paraffins. Occurrence in Lava.—A lava from Paternò, at the foot of Etna, was found by O. Silvestri (*Gazz. chim. ital.* 1877, 1) to contain a petroleum (1 per cent. of the rock) yielding 42.79 per cent. of solid paraffin, together with 17.97 per cent. of a liquid hydrocarbon boiling at 280°, 31.95 per cent. of another boiling at 280°-400°, together with 2.90 per cent. asphalt, 12 ash, and 4.39 sulphur.

Purification.—Fordred (*Monit. scient.* [3], iii. 826) purifies crude paraffin by melting it, leaving the mechanical impurities to settle down to the bottom of the liquid mass, and then transferring it to small vessels to cool. The cakes are next warmed again till they become kneadable, and in this state the paraffin is finally washed with a solution of 10 pts. soft soap in 90 water, and heated to about 38° C. The colouring matters, and any oils that may be present, are transferred by this treatment to the soap-water, and the solid paraffin comes out purified and bleached.

An apparatus for decolorising paraffin by means of pulverised animal charcoal is described by L. Rahmdohr (*Dingl. pol. J.* ccxvi. 244).

On the Estimation of Paraffin in Stearin-candles, see Donath (*Dingl. pol. J.* ccviii. 305; *Chem. Soc. J.* xxviii. 1058).

Specific Gravity.—The sp. gr. of paraffin in the solid and fused states has been determined by Albrecht (*Dingl. ccxviii.* 280), with the following results:

	Melting point	Specific gravity		
		at 17°	at 55°	at 60°-65°
Solar oil and Paraffin . . .	38°	0.872	0.779	—
Secunda Paraffin . . .	43	0.883	0.788	—
Secunda Press-paraffin . . .	43	0.889	0.785	—
Secunda Paraffin . . .	46	0.887	—	0.781
Prima Press-paraffin . . .	47	0.900	—	0.775
Prima Paraffin . . .	51	0.908	—	0.775
Hard "Paraffin" . . .	56	0.912	—	0.777

These numbers show that paraffins expand considerably in melting. Albrecht also observed that solutions of paraffin in mineral oils have lower specific gravities than either the oils and the paraffins separately, so that in selecting for technical purposes lubricating oils of as great a density as possible, it is best to take paraffin oils from which the greater part of the solid paraffin has crystallised out.

Oxidation.—When paraffin is exposed for some time at 120° to a stream of air or oxygen, an absorption of that gas takes place. The same action takes place with coal, and may explain the increase of weight often observed when coal is dried in heated air (Jaznowitsch, *Ber.* viii. 768).

G. Pouchet (*Compt. rend.* lxxix. 320) finds that paraffin (m. p. not stated), treated with fuming nitric acid at a temperature not exceeding 110°, till it assumes a buttery consistence, yields a product from which water extracts butyric, valeric, caproic, cœnanthyl, caprylic, capric, and suberic acids, together with nitrated fatty acids, chiefly nitrocaprylic and nitrocapric. When a mixture of sulphuric and nitric acids is used, the product yields to water nothing but suberic acid, and a peculiar deliquescent crystalline acid soluble in water and alcohol, while the portion insoluble in water consists of a solid acid called by Pouchet *paraffinic acid*, which, when purified by saponification, &c., has the composition $C^{24}H^{40}O_2$, whence it may be inferred that the particular paraffin operated on consisted of $C^{24}H^{40}$. Paraffinic acid is described as a whitish-yellow solid, smelling like wax, easily decomposed by heat, and burning with a bright smoky flame; insoluble in water, moderately soluble in dilute, easily in strong alcohol, also in ether, chloroform, benzene, and petroleum, and separating from the alcoholic solution by slow evaporation in nacreous laminae. Nitric acid converts

it into suberic acid and nitro-derivatives of fatty acids. Heated with potash lime, it yields paraffins, solid and liquid, together with olefines.

Gill a. Meusel, by oxidising paraffin (m. p. 66°) with chromic acid mixture, obtained cerotic acid (vi. 421). This acid was not observed by Pouchet amongst the products of oxidation with nitric acid.

NITROPARAFFINS.

Nitromethane, CH^3NO^2 . This compound, already described in vol. vii. p. 893, has been further examined by Preibisch (*J. pr. Chem.* [2], vii. 480; viii. 309). In preparing it by heating potassium monochloracetate with potassium nitrite (Kolbe's method), the result is the same whether the solutions are concentrated or dilute, the only difference being that in the latter case the liquid does not froth so much. Among the secondary products ammonium carbonate was found, the presence of which caused the blackening of the liquid and the loss of nitromethane.

Dry ammonia does not act on nitromethane, but aqueous ammonia dissolves it, the liquid soon darkening, and carbon separating out. When a little water is added to a mixture of alcoholic ammonia and nitromethane, and the solution is evaporated under the exsiccator, a small quantity of fine brownish needles is obtained, which soon undergo complete decomposition, even if kept in a closed tube. Nitromethane, heated with iron-filings, acetic acid, and water, is converted into methylamine.

The sodium-compound, CH^2NaNO^2 , is conveniently prepared by precipitating an alcoholic solution of nitromethane with alcoholic soda, and washing the precipitate once with alcohol on the filter-pump. In the moist state it soon turns yellow, and it is therefore advisable to use only a small quantity of nitromethane for each operation. With an alcoholic turmeric solution it produces a deep-red colour. Sodium-nitromethane acts violently on acid chlorides, but no definite compounds could be obtained; neither was an isomeride of nitrotoluene formed by acting on it with bromobenzene. Chlorine and bromine do not act on nitromethane, even in sunshine, whereas by leaving it in contact with a mixture of nitric acid and sulphuric acid for some weeks, a body was formed exploding most violently on distillation. When nitromethane is mixed with *bleaching powder* and a little water, a brisk evolution of gas sets in, and chloronitromethane, CH^2ClNO^2 , distils over. This compound boils at 98° and has a very pungent and irritating smell. The corresponding bromine-compound could not be obtained in the pure state. Nitromethane is not acted upon by phosphorus pentoxide, or by concentrated sulphuric acid; but, on heating it gently with *fuming sulphuric acid*, a violent reaction sets in, carbon monoxide and sulphur dioxide being given off, and hydroxylamine sulphate produced: $\text{CH}^3\text{NO}^2 = \text{CO} + \text{NH}^3\text{O}$ (p. 1074). Heated with *hydrochloric acid* (sp. gr. 1.14), best in a sealed tube at 150° , it yields hydroxylamine and formic acid, $\text{CH}^3\text{NO}^2 + \text{H}^2\text{O} = \text{NH}^3\text{O} + \text{CH}^2\text{O}^2$ (Meyer a. Locher, *Ber.* viii. 219). By heating with an alcoholic solution of caustic soda, nitromethane is converted into the sodium salt of methazonic acid, $\text{C}^2\text{H}^4\text{N}^2\text{O}^3$ (p. 1301).

On *mono-bromonitromethane*, formed by the action of bromine on sodium-nitromethane, and *dibromonitromethane*, produced from it by the action of bromine and potash-ley, see Tscherniak (vii. 894).

Nitroethane, $\text{C}^2\text{H}^5\text{NO}^2$. This compound, gently heated with *fuming sulphuric acid*, is converted into ethylene-disulphonic acid, $\text{C}^2\text{H}^4(\text{SO}^2\text{H})^2$ (p. 755). *Hydrochloric acid*, of sp. gr. 1.14, acts upon it in the same manner as on nitromethane, yielding hydroxylamine and acetic acid. According to Werner (*Jen. Zeitschr.* [2], iii. 2nd Suppl. 70), the same reaction is also produced by sulphurous acid.

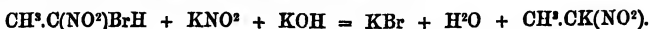
When potassium nitro-ethane, $\text{C}^2\text{H}^4\text{K}(\text{NO}^2)$, is added to solution of *diazobenzene nitrate* (obtained by adding nitraniline to a dilute solution of potassium nitrite, and filtering from a yellow insoluble compound formed at the same time), a yellow acid body is precipitated having the composition $\text{C}^4\text{H}^8\text{N}^4\text{O}^4 = \text{C}^4\text{H}^4\text{NO}^2.\text{N}^2.\text{C}^2\text{H}^4\text{NO}^2$. This body forms, when pure, a yellow powder soluble with red colour in alkalis, and easily soluble in hot alcohol. The sodium salt is sparingly soluble in water; its solution gives coloured precipitates with silver, copper, and lead salts. When treated with tin and hydrochloric acid, the acid yields a body which forms with stannic chloride a crystalline compound agreeing in composition with the formula $\text{C}^4\text{H}^{16}\text{N}^4\text{Cl}^2.\text{SnCl}^4$. The formation of this body may perhaps be represented by the equation $\text{C}^4\text{H}^8\text{N}^4\text{O}^4 + \text{H}^{14} + 2\text{HCl} = 4\text{H}^2\text{O} + \text{C}^4\text{H}^{16}\text{N}^4\text{Cl}^2$ (Hallmann, *Ber.* ix. 389).

When *diazobromobenzene nitrate* (obtained by adding potassium nitrite to a solution of parabromaniline in nitric acid) is mixed with potassium-nitroethane, a precipitate is formed, having the composition $\text{C}^8\text{H}^{12}\text{Br}.\text{N}^2.\text{C}^2\text{H}^5(\text{NO}^2)\text{K}$. This salt separates from alcoholic solution in shining brick-red crystals soluble in ether, chloroform, &c., melting with decomposition at 136° – 138° . Its solution gives with cupric sulphate a greenish-yellow precipitate, with lead acetate a light red precipitate, and with silver

nitrate a precipitate of a deep orange colour soon turning black (H. Wald, *Ber.* ix. 393).

On *Bromo- and Dibromonitroethane*, see vii. 805.

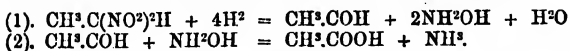
Dinitroethane, $C^2H^4(NO^2)^2 = CH^3.CH(NO^2)^2$ (E. ter Meer, *Ber.* viii. 793, 1080). The potassium-derivative of this compound is formed by the action of potassium nitrite and alcoholic potash on monobromonitroethane:



It is best prepared by dissolving 21 grams of monobromonitroethane in twice its weight of alcohol, and adding first a solution of 12 grams potassium nitrite in the same weight of water, and then gradually 45 pts. of alcoholic potash (1 : 5). After standing for one to two hours, the crystals which have separated out are first washed with alcohol and ether, and then with water to remove the potassium bromide. On adding a dilute acid to the potassium compound, dinitroethane separates out as a colourless, very refractive liquid, having a peculiar sweet taste, and a faint alcoholic smell. It boils at 185° – 186° (cor.), and has, at 23.5° , the sp. gr. 1.3503. It is a tolerably strong acid, which even decomposes carbonates, though not readily. The *potassium salt* forms yellow glistening monoclinic crystals, $a : b : c = 0.58124 : 1 : 0.99016$. It is sparingly soluble in cold water, readily in hot water, and insoluble in absolute alcohol; when exposed to light it acquires an orange colour. The *sodium salt* is a very similar body, but dissolves more freely in water and alcohol. The *barium salt* crystallises in yellow needles or small plates; and the very explosive *silver salt*, $CH^3.C(NO^2)^2Ag$, forms small yellow plates having a metallic lustre and dissolving but sparingly in water.

The aqueous solution of the potassium salt is not precipitated by calcium, barium, strontium, aluminium, cobalt, or ferrous salts. Ferric chloride forms a reddish-brown precipitate; lead acetate a pure yellow crystalline precipitate; basic lead acetate a bulky yellow precipitate; copper sulphate a pale blue; and mercuric chloride a light brown precipitate. Mercurous nitrate produces a greyish-black precipitate, soon changing into colourless crystals.

By reduction with *tin and hydrochloric acid*, dinitroethane ought to yield aldehyde and hydroxylamine, seeing that dinitropropane, as shown by Meyer (*infra*), yields by reduction hydroxylamine and acetone. But only a trace of aldehyde was actually obtained, the products being acetic acid, ammonia, and hydroxylamine. This is easily explained on the supposition that the aldehyde in the nascent state is oxidised by hydroxylamine, and this was confirmed by experiment. On passing the vapour of aldehyde mixed with carbon dioxide into a boiling solution of pure hydroxylamine hydrochloride containing a little freshly prepared spongy platinum, the hydroxylamine was soon reduced to ammonia. The reactions which take place in the reduction of dinitroethane may therefore be represented by the following equations:



Monobromodinitroethane, $CH^3.CBr(NO^2)^2$, is produced on adding bromine-water to an aqueous solution of potassium-dinitroethane, and separates as a heavy colourless oil having a highly pungent odour. It decomposes when distilled alone, but volatilises undecomposed with steam. By *potash* either in aqueous or alcoholic solution, and even by *potassium carbonate*, it is decomposed, with evolution of oxygen and reproduction of potassium dinitroethane:



Nitro-allylethane, $C^3H^4(C^2H^3).NO^2$, appears to be formed on adding allyl iodide to a solution of nitroethane in a quantity of alcoholic potash sufficient for the production of potassium-nitroethane. A brisk reaction then takes place, attended with separation of potassium iodide, and the filtrate, when mixed with water, deposits an oil which cannot be distilled without decomposition. This oil, reduced with zinc and hydrochloric acid, yields a liquid amine which boils at 85° , dissolves in water and in alcohol, is separated from the aqueous solution by potash, reacts strongly with carbon disulphide, but does not form with it a crystallisable compound. The platinum-chloride of this amine crystallises from water in yellow laminae, and gives by analysis a quantity of platinum, indicating that the formula of the amine is $C^3H^5.NH^2$. Hence it is probable that the oily nitro-compound from which the amine is formed is nitro-allylethane, $C^3H^5.NO^2$ (H. Gal, *Compt. rend.* lxxvi. 1354).

Nitropropanes. Normal nitropropane, $CH^3.CH^2.CH^2(NO^2)$, formed by the action of propyl iodide on silver nitrite (vii. 895), boils, according to Cahours (*Compt. rend.* lxxvii. 749), at 125° – 128° , and burns with a yellowish flame. By *nascent*

hydrogen it is converted into propylamine; by *alcoholic soda* into the sodium salt, $C^3H^5Na(NO^2)$, which crystallises in laminæ slightly soluble in alcohol.

Normal nitropropane is decomposed by dilute *hydrochloric acid* in the same manner as nitroethane (p. 1490), yielding hydroxylamine and propionic acid. Isomeric nitropropane, on the other hand, is converted by hydrochloric acid into a black-brown greasy substance containing a large quantity of ammonium chloride (Meyer a. Locher, *Ber.* viii. 219).

On *Bromonitropropanes*, see Meyer a. Tscherniak (vii. 896).

Dinitropropane, $C^3H^5(NO^2)^2$. Of this compound two modifications are known, distinguished as α and β .

α -*Dinitropropane*, $CH^3.CH^2.CH(NO^2)^2$, is obtained by treating 27 pts. of normal monobromonitropropane, $CH^3.CH^2.CHB(NO^2)$, with 27 pts. alcohol and 28 pts. of an aqueous solution of potassium nitrite (1 : 1), and immediately adding 54 pts. of alcoholic potash (5 : 1), and separating the resulting potassium α -dinitropropane, $CH^3.CH^2.C(NO^2)^2K$, from the potassium bromide which is deposited at the same time, by recrystallisation from hot water. This salt forms light yellow explosive laminæ, resembling those of dinitroethane, easily soluble in hot water, insoluble in absolute alcohol and in ether. On adding it (either pure or in the crude state mixed with potassium bromide) to dilute sulphuric acid, α -dinitropropane is obtained as a colourless, nearly scentless oil, having a density of 1.258 at 22.5°, remaining liquid at -17°, and boiling at 189° (corr. 192.5°). It forms coloured precipitates with salts of the heavy metals. The *silver salt*, $CH^3.CH^2.C(NO^2)^2Ag$, forms greenish-yellow explosive laminæ (E. ter Meer, *Ber.* viii. 793 and 1080).

β -*Dinitropropane*, $CH^3.C(NO^2)^2.CH^3$, is obtained by oxidation of propyl-pseudonitrole, $CH^3.C(NO)(NO^2).CH^3$. For this purpose 2 pts. of dry finely pulverised propyl-pseudonitrole are drenched with 16 parts of glacial acetic acid, and $\frac{1}{4}$ pts. chromic acid are added, the liquid being at the same time gently heated, so that the reaction-temperature may not exceed 76°. When the action is complete, the mixture is poured into water, the acetic acid neutralised with aqueous alkali, and the product of the reaction separated either by extraction with ether or by distillation with steam. This same compound is produced in small quantity in the decomposition of propyl-pseudonitrole by heat. After distillation with steam and drying over calcium chloride, it forms dazzling-white crystals melting at 53°; it boils without decomposition at 185.5°. The crystals sublime below their melting point; volatilise easily with vapour of water; deliquesce in alcohol, ether, and glacial acetic acid; dissolve but sparingly in water, and not at all in aqueous alkalis (Meyer a. Locher, *Ber.* vii. 1613).

Nitrobutanes. Normal nitrobutane, $CH^3.CH^2.CH^2.CH^2(NO^2)$, prepared by the action of silver nitrate on well-cooled normal butyl iodide, is a colourless liquid, lighter than water, distilling without decomposition at 151°-152°, soluble in caustic potash. It is easily converted into butylamine by the action of tin and hydrochloric acid; resolved by heating with hydrochloric acid to 140° into hydroxylamine hydrochloride and normal butyric acid; converted by nitrous acid into normal butylnitric acid.

Normal monobromonitrobutane, $CH^3.CH^2.CH^2.CHB(NO^2)$, prepared by the action of bromine on normal potassium-nitrobutane, is a heavy oil, boiling at 180°-181°. The *dibromonitrobutane* obtained by the action of bromine on a mixture of normal nitrobutane and caustic potash, is a heavy, yellow oil, insoluble in caustic potash, boiling at 203°-204° (J. Züblin, *Ber.* x. 2083).

Normal dinitrobutane, $C^4H^9(NO^2)^2$, is prepared by slowly adding dilute sulphuric acid to a mixture of potassium nitrite and normal monobromonitrobutane dissolved in excess of caustic potash, until a blue colour is produced. Caustic potash is then added, the resulting potassium dinitrobutane acidified with sulphuric acid, and the dinitrobutane extracted with ether. It is a yellow oil, boiling at 190°, but decomposed by distillation. The potassium salt forms brilliant golden scales, soluble in water and in alcohol. The aqueous solution gives with silver nitrate a precipitate of silver-dinitrobutane, which can be obtained by recrystallisation in large scales, appearing yellow by transmitted and bluish violet by reflected light.

Normal monobromodinitrobutane, $C^4H^9.CBr(NO^2)^2$, obtained by acting on potassium dinitrobutane with bromine-water, is an oily liquid, decomposed by distillation (Züblin, *loc. cit.*)

Isonitrobutane, $(CH^3)^2CH.CH^2(NO^2)$, which Demole obtained by the action of silver nitrite on isobutyl iodide, has been already described (vii. 897). *Isobromonitrobutane*, $(CH^3)^2CH.CHB(NO^2)$, is a heavy oil, boiling at 173°-176°, and otherwise resembling its isomeride.

Isodinitrobutane, $(\text{CH}^3)_2\text{CH}.\text{CH}(\text{NO}^2)_2$, is a yellowish oil decomposing when distilled. Its potassium and silver salts crystallise in yellow shining needles. *Isobromodinitrobutane*, $(\text{CH}^3)_2\text{CH}.\text{CBr}(\text{NO}^2)_2$, is obtained by the action of bromine-water on an aqueous solution of potassium-isodinitrobutane, and purified by treatment with sulphurous acid to remove free bromine, washing with caustic soda, and distillation in a current of steam. It is a colourless vitreous body, resembling camphor in appearance, having a pungent odour, and melting at 38° . Its potassium salt, treated with diazobenzene nitrate, yields *isonitrobutyl-azophenyl*, $\text{C}^6\text{H}^5.\text{N}=\text{N}.\text{CH}(\text{NO}^2)\text{CH}(\text{CH}^3)_2$, as a yellowish oil, dissolving with yellow-red colour in alkalis (Züblin).

Secondary Nitrobutane, $\text{CH}^3.\text{CH}^2.\text{CH}(\text{NO}^2).\text{CH}^3$, is prepared by the action of secondary butyl iodide (120 pts.) on silver nitrite (150 pts.), the latter being mixed with an equal weight of previously ignited sand. The reaction is attended with considerable rise of temperature; normal butylene is given off; and the residual mass consists of a mixture of secondary nitrobutane and butyl nitrite, which are but imperfectly separable by fractional distillation. The nitrobutane (not quite pure) thus obtained is a colourless oil having a peculiar odour, boiling at about 140° , and converted by repeated agitation with potash and potassium nitrite into butyl-pseudonitrole, $\text{CH}^3.\text{CH}^2.\text{C}(\text{NO})(\text{NO}^2).\text{CH}^3$ (V. Meyer & Locher, *Ber.* vii. 1506).

Tertiary nitrobutane, $(\text{CH}^3)_3.\text{C}(\text{NO}^2)$, is formed in small quantity, together with butyl nitrite and oxides of nitrogen, by the action of silver nitrite on tertiary butyl iodide. It is a colourless liquid, smelling like peppermint and boiling between 110° and 130° . Like nitrobenzene, it has no acid properties, the carbon-atom to which the NO^2 -group is attached not being also combined with a hydrogen-atom. Accordingly it does not yield a bromo-derivative when treated with bromine and potash; neither is it converted into a pseudonitrole by treatment with dilute sulphuric acid, potassium nitrite, and potash (Tscherniak, *Liebigs Annalen*, clxxx. 155).

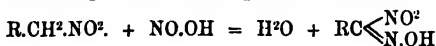
Nitrolic Acids and Pseudonitroles.

(1). The nitrolic acids, $\text{C}^n\text{H}^{2n}\text{N}^2\text{O}^3$, may be represented by either of the two following constitutional formulæ, in which R stands for $\text{C}^n\text{H}^{2n+1}$, n having any integral value from 0 upwards:

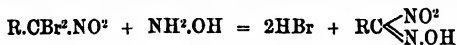


The first of these formulæ agrees best with the modes of formation of the nitrolic acids, the second with their decomposition by heat and by sulphuric acid.

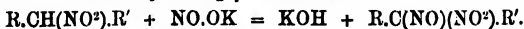
Nitrolic acids are produced: 1. By the action of nitrous acid, or better of potassium nitrite and sulphuric acid, on the sodium derivatives of primary nitro-paraffins, or on solutions of these nitro-compounds in caustic potash or soda:



2. By the action of the dibrominated nitroparaffins on hydroxylamine:



(2). Pseudonitroles, $\text{C}^n\text{H}^{2n+1}.\text{C}(\text{NO})(\text{NO}^2).\text{C}^n\text{H}^{2n+1}$, are formed by the action of potassium nitrite on secondary nitro-paraffins, thus:



Methyl-nitrolic Acid, $\text{CH}^3\text{N}^2\text{O}^3 = \text{H}(\text{NO}^2)\text{C}=\text{N.OH}$. This acid is very unstable in aqueous solution, so that its preparation requires special precautions. The following method is given by Tscherniak (*Ber.* viii. 114): Nitromethane (15 grams) is treated with a quantity of water just sufficient to dissolve it, and the solution is mixed with a moderately dilute solution of potassium nitrite (8 grams) and cooled to 0° by addition of a large quantity of ice. A mixture of sulphuric acid (4 grams) with a large quantity of water is also cooled by ice, and slowly poured into the first liquid, to which, thus diluted, weak aqueous potash is first added till it turns red, and then again dilute sulphuric acid till the colour disappears. To remove any free nitrous acid, the solution is shaken with a little precipitated chalk, after which the nitrolic acid is dissolved out by ether, and the solution evaporated over sulphuric acid.

Methylnitrolic acid thus obtained forms large brittle crystals resembling the ethyl-compound; from a dilute ethereal solution it separates in long needles. It decomposes slowly at ordinary temperatures, rapidly at 64° , into formic acid, nitrogen, and nitrogen tetroxide:



By boiling with dilute sulphuric acid, it is resolved into formic acid and nitrogen monoxide:



Ethylnitrolic Acid, $\text{C}^2\text{H}^4\text{N}^2\text{O}^3 = \text{CH}^3(\text{NO}^2)\text{C}=\text{N}.\text{OH}$ (V. Meyer a. Locher, *Ber.* vi. 1494; Meyer, *ibid.* vii. 425). The preparation of this compound by the action of potassium nitrite and sulphuric acid on an alkaline solution of nitroethane has been already described (vii. 564). It is essential that the nitroethane be first dissolved in the alkali; for if the nitroethane and sulphuric acid be added simultaneously to a solution of potassium nitrite, no ethylnitrolic acid will be produced.

Ethylnitrolic acid crystallises in light yellow, transparent, highly lustrous prisms, very much like saltpetre; by slow evaporation of the aqueous or ethereal solution it is easily obtained in crystals an inch long. According to Kennigott's measurements, they belong to the orthorhombic system, exhibiting the combination $\infty P.\infty \bar{P}.\infty \bar{P}.\infty$. The angle of the brachydiagonal prismatic edge is approximately $108^\circ 30'$; that of the terminal edge of the transverse dome $47^\circ 30'$. The acid has a strong sweet taste and acid reaction. It dissolves readily in all the ordinary solvents, and its difference of solubility in cold and slightly warm water is so great that a solution saturated merely at the heat of the hand deposits an abundant crop of crystals a few minutes after the hand has been removed.

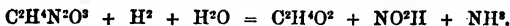
The ethylnitrolates of sodium, potassium, ammonium, and barium dissolve in water, with a deep red colour, but have not been obtained in the pure state. Water is required for their formation, inasmuch as nitroethane dissolves in an ethereal solution of ammonia without coloration, but on adding a trace of water, the liquid assumes a deep red colour. The action of alkalis on ethylnitrolic acid is so sensitive that this acid might be used as an indicator in alkalimetry. The ethylnitrolates of the heavy metals are coloured unstable precipitates, very easily changing into nitrites. The lead salt has a brilliant orange colour, and the silver salt is egg-yellow.

Ethylnitrolic acid, heated to $80^\circ\text{--}81^\circ$, melts and suffers rapid decomposition, giving off nitrogen tetroxide and free nitrogen, and leaving glacial acetic acid:



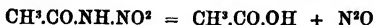
The same decomposition goes on slowly at the common temperature, and quickly on boiling with an alkali. In these decompositions a small quantity of a white solid, containing nitrogen and melting at 61° , is always formed.

Nascent hydrogen obtained from tin and hydrochloric acid or sodium-amalgam, converts the acid into acetic acid, nitrous acid, and ammonia—



Strong sulphuric acid, when employed in excess in order to moderate the reaction, decomposes it into acetic acid and nitrogen monoxide: $\text{C}^2\text{H}^4\text{N}^2\text{O}^3 = \text{C}^2\text{H}^4\text{O}^2 + \text{N}^2\text{O}$.

These decompositions are most readily explained on the supposition that ethyl-nitrolic acid contains the radicle acetyl, as represented by the second of the two general formulæ on p. 93, *e.g.*



(Victor Meyer, *Ber.* vii. 425).

Propyl-nitrolic Acid, $\text{C}^3\text{H}^5\text{N}^2\text{O}^3 = \text{CH}^3.\text{CH}^2(\text{NO}^2)\text{C}=\text{N}.\text{OH}$, may be prepared either by passing nitrous acid into a solution of nitropropane in potash, and adding sulphuric acid, or by the action of dibromonitropropane on hydroxylamine. Hydroxylamine hydrochloride (7 pts.), dissolved in a small quantity of water, is decomposed with the exact quantity of baryta-water required, and dibromonitropropane (2 pts.) prepared from primary nitropropane is added to the mixture; the mass, after being left to itself two days at the ordinary temperature and frequently shaken, is acidulated with sulphuric acid and agitated with ether; the resulting ethereal solution is purified by mixing it with soda-ley, acidulating with sulphuric acid, and exhausting with ether; and the propyl-nitrolic acid which remains after the evaporation of the ether is finally purified by once recrystallising it from the same solvent (Meyer a. Lecco, *Ber.* ix. 395).

Propyl-nitrolic acid crystallises in light yellow prisms having a sweet and biting taste, easily soluble in water, alcohol, and ether, coloured deep red by alkalis, melting at 60° , and decomposing at higher temperatures with violent evolution of red vapours. By sodium-amalgam and water it is resolved into ammonia, nitrous acid, and probably also propionic acid; by strong sulphuric acid into propionic acid and nitrogen monoxide. When left to itself in a sealed tube it begins to decompose in four or five weeks; on subsequently opening the tube, red fumes escape with vio-

lence, and the residual liquid is found to consist of propionic acid. The metallic *propylnitrolates* quickly decompose in the same manner as the ethylnitrolates, yielding nitrites (V. Meyer, *Liebig's Annalen*, clxxv. 114).

Propylpseudonitrole, $\text{CH}^3\text{C}(\text{NO})(\text{NO}^2)\text{CH}^3$. When an alkaline solution or secondary nitropropane is treated with potassium nitrite and sulphuric acid, the liquid assumes a fine deep blue colour, and propylpseudonitrole is separated in the form of a white sandy powder. This compound, isomeric with propylnitrolic acid, is insoluble in water, alkalis and acids, not very freely soluble in cold alcohol or chloroform, but readily in the hot liquids, forming blue solutions from which it crystallises on cooling. By slow evaporation from the chloroform solution it is obtained in large colourless glassy monoclinic crystals, having the axial ratio $a : b : c = 1.2911 : 1 : 0.6672$. It melts at 76° to a deep blue liquid, which solidifies on rapid cooling to a colourless mass, but when further heated, is converted, with brisk evolution of gas, into an oil which no longer solidifies. When suspended in water it is not acted upon by sodium-amalgam in presence either of acid or of alkali, but in alcoholic solution it is decomposed by sodium-amalgam, with decolorisation, and formation of sodium nitrite and a white flocculent sodium-compound. When gently heated with strong sulphuric acid, it gives off a large quantity of a gas which extinguishes flame. It is partially decomposed by boiling water, and when heated with aqueous alkalis it gives off nitrogen, and forms a nitrate. By oxidation with chromic acid it is converted into dinitropropane, $\text{CH}^3\text{C}(\text{NO}^2)^2\text{CH}^3$ (p. 1492), (Meyer, *Liebig's Annalen*, clxxv. 120).

Butylnitrolic Acid, $\text{C}^4\text{H}^7\text{N}^2\text{O}^3 = \text{C}^4\text{H}^7(\text{NO}^2)\text{C}=\text{N.OH}$, obtained by the action of potassium nitrite and sulphuric acid on an alkaline solution of primary nitrobutane, is not crystallisable, but remains as a syrup on evaporation of its ethereal solution. It forms red alkaline solutions, and yields with silver nitrate an orange-coloured precipitate which quickly decomposes with formation of nitrite. By strong acid, it is resolved into isobutyric acid and nitrogen monoxide (Demole, *Ber.* vii. 790).

Butylpseudonitrole, $\text{C}^4\text{H}^8\text{C}(\text{NO})(\text{NO}^2)\text{CH}^3$, is obtained by repeatedly agitating secondary nitrobutane with potassium nitrite and potash-ley as long as it continues to dissolve, removing the oil (isobutyl nitrite) which floats on the surface of the liquid, and mixing the alcoholic solution with dilute sulphuric acid, whereby the pseudonitrole is separated as a blue liquid solidifying on cooling to a nearly colourless mass which may be purified by triturating it with dilute potash-ley, then washing it with water, and dried by aid of heat. Butylpseudonitrole resembles the corresponding propyl-compound in its relations to solvents, and in being white in the solid, blue in the liquid state, but differs from it by melting at a lower temperature, namely, at 58° (Meyer, *Ber.* vii. 1506).

The modes of formation and the colour-reactions of the nitrolic acids and pseudonitroles may be utilised as a means of distinguishing between primary, secondary and tertiary alcohols of the series $\text{C}^n\text{H}^{2n+1}\text{OH}$. Since the formation of nitrolic acids is determined by the presence of the group CH^2NO^2 , and that of pseudonitroles by the group CH.NO^2 , and consequently the tertiary nitro-derivatives of the fatty series cannot give rise either to nitrolic acids or to pseudonitroles, it follows that the three classes of alcohols may be distinguished by the following reactions. A quantity of dry silver nitrite, mixed with an equal weight of previously ignited sand, is introduced into a small distillation-flask fitted with a side-tube; the hydriodic ether of the alcohol under examination is then added; the mixture, after the reaction has begun, is distilled over an open flame without a condenser; and the distillate, received in a test-tube, is shaken up with potassium nitrite and potash-ley, and then acidulated with dilute sulphuric acid. If no coloration of the mass ensues, the alcohol-radicle present is a tertiary, whereas a red coloration indicates the presence of a primary, and a blue coloration that of a secondary radicle. The reaction may be recognised with great distinctness with the use of not more than 0.3 to 0.5 grm. of the alcoholic iodide (Meyer a. Locher, *Ber.* vii. 1510).

PARAGLOBULIN. See PROTEIDS.

PARAGUAY TEA or **MATÉ**. This substance, the produce of the *Ilex paraguayensis* or *Ilex Maté* of South America, where a decoction of it constitutes a favourite drink, has been examined by H. Byasson (*Pharm. J. Trans.* [3], viii. 605). The variety examined was the greenish-yellow powder, which is prepared by the natives from the roasted and coarsely-powdered leaves. The analysis was

made by mixing the maté with lime and successively exhausting the mixture with chloroform and alcohol. 100 grams gave :—

Caffeine	1.85
Glutinous substance, &c.	3.87
Complex glucoside	2.38
Resin	0.63
Inorganic salts, including iron	3.92
Malic acid	not estimated.

Exhausted with boiling water, the tea gave 24 per cent. dry extract, and 3.02 per cent. of ash in the extract, calculated on the maté taken. The ash contained potassium carbonate and much sulphuric acid. The tests for tannin and caffeic acid gave negative results. The amount of caffeine is comparable with that in the kinds of tea and coffee richest in that alkaloid.

PARAHYDROCYANALDINE, $C^8H^{12}N^4$. The crystalline forms of this compound, and of its isomeride hydrocyanaldine (i. 108), have been examined by C. Haushofer (*Zeitschr. Kryst.* i. 620). Hydrocyanaldine crystallises in the monoclinic system; $a : b : c = 2.8727 : 1 : 3.8596$; angle $ac = 52^\circ 28'$. The crystals, which are for the most part well developed on all sides, exhibit the combination $\infty P . 0P . \infty P \infty . + P \infty . - \frac{1}{2}P \infty$. The orthopinacoid faces exhibit striation, parallel to the combination-edge with $-\frac{1}{2}P \infty$. The crystals do not exhibit any distinct cleavage. They are permanent in the air, and melt at 115° .

Parahydrocyanaldine forms orthorhombic crystals having the axial ratio $a : b : c = 0.6639 : 1 : 1.8741$. Observed combination $\infty P . \infty P \infty . P \infty . 0P$; prismatic in the direction of ∞P ; more rarely tabular in that of $\infty P \infty$. Melting point 230° – 232° .

PARAISOBUTYRIC ALDEHYDE, $C^{12}H^{24}O^2$. This polymeric compound, which Barbaglia obtained by the action of chlorine on isobutyric aldehyde (vii. 228), is likewise produced by the action of bromine or iodine. Bromine acts best in the form of vapour mixed with air. Cyanogen has no effect (Barbaglia, *Ber.* vi. 1064). The same polymeric modification is produced by the action of phosphorus pentachloride on isobutyric aldehyde, its formation in this case being probably due to the small quantity of hydrochloric acid formed from the pentachloride by the action of moisture, for strong sulphuric acid and gaseous hydrogen chloride likewise bring about the polymerisation; on bringing the substances together great heat is evolved, and the liquid solidifies on cooling to a crystalline pulp of slender needles (Demtschenko, *ibid.* 1176). It melts at 60° , resolidifies at 50° – 51° , and is not altered by heating to 200° in a sealed tube for 15 hours, or by dry chlorine, bromine, or iodine (Barbaglia). Boils at 194° . Crystallises in needles from water, and on sublimation (Demtschenko).

PARALACTIC ACID. See LACTIC ACIDS (p. 1160).

PARALBUMIN. See PROTEIDS.

PARALDOL. See ALDOL (p. 54).

PARAMORIN. See MORIN (p. 1336).

PARA-NUTS. These nuts contain crystallised vitellin. See PROTEIDS.

PARARABIN. See ARABIN (p. 119).

PARICINE, $C^{14}H^{18}N^2O$. This alkaloid, occurring together with quinamine in the bark of *Cinchona succirubra* from Darjeeling, may be separated from all the cinchona-alkaloids with which it may be associated in a saline solution, by means of sodium carbonate, which throws it down before any of the rest (Hesse, *Ber.* x. 2152).

PARIGENIN and PARILLIN. Substances allied to SAPONIN (q. v.)

PASSYTE. A white earthy silicious mineral, occurring in layers or kidney-shaped masses at the border of the red clays and argillaceous sands which overlie the chalk in the Department of the Seine inférieure, frequently also enveloping flints. Analysis by Marchand (*Ann. Chim. Phys.* [5], i. 392):

H ² O	SiO ²	CaCO ³	MgCO ³	Fe ² O ³ , Al ² O ³
1.1	84.5	15.0	trace	— = 100.6
0.3	89.2	10.4	trace	trace = 99.9
—	88.9	11.4	trace	— = 100.3

PASTINACA. The volatile oil of the fruit of the parsnip (*Pastinaca sativa*) contains the normal butyric ether of normal octyl alcohol.

PASTINACINE. A volatile alkaloïd, existing, according to Wittstein (iv. 357), in the seeds of the parsnep, and, according to A. R. Porter (*Pharm. J. Trans.* [3], vii. 174), in the root of *Sium latifolium*.

PATCHOULI CAMPHOR, $C^{15}H^{20}O$. This substance, first examined by Gall (vi. 902), who assigned to it the formula $C^{15}H^{20}O$, has been further investigated by J. de Montgolfier (*Compt. rend.* lxxxiv. 88; *Ber.* x. 234). It forms regular hexagonal crystals, some almost spherical from the rounding of the faces. They are always composed of a prism and a pyramidal summit, and do not exhibit hemihedry. The inclination of the faces to each other is 120° , and to the summit $120^\circ 24'$. They have no rotatory power for polarised light; but the liquid camphor is lævogyrate; $[\alpha]_D = -118^\circ$. The rotatory power remains constant when the camphor is dissolved in alcohol of 95 per cent., but diminishes considerably on dilution. If e be the proportion by weight of substance in solution:

$$(\alpha)_D = -124^\circ 5' + 21 e.$$

The dispersion is nearly the same as that of quartz or of sugar; $[\alpha]_D = -10^\circ 37'$ and $\alpha_D = -11^\circ 45'$. The crystals melt at 52° and remain liquid for a long time.

The corresponding hydrocarbon, *Patchoulin*, $C^{15}H^{22}$, is easily prepared from the camphor by the action of acids, but the best method is to heat the camphor to 100° for some hours with a mixture of glacial acetic acid and acetic anhydride. The upper layer consists of the hydrocarbon. It boils at 252° – 255° under 743 mm. pressure. It has no smell when pure, but oxidises easily and then acquires a resinous odour. Its density is 0.946 at 0° , and 0.937 at 13.5° . It turns the plane of polarised light strongly to the left; -7.45° for the line D, and -8.48° for the transition tint. Its dispersion is therefore equal to that of quartz, and its molecular rotatory power is $(\alpha) = -42^\circ 10'$. It does not combine with hydrochloric acid, and is destroyed by nitric acid. It most resembles essence of cubebs, but differs from it in not combining with hydrochloric acid.

PATTERSONITE. A variety of margarite accompanying corundum from Unionville, Pennsylvania. Sp. gr. = 2.81. Analysed by Genth (*Jahresb. f. Chem.* 1873, 1158):

SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	Na ² O	K ² O	Loss by ignition
29.90	27.59	3.12	9.17	17.10	0.58	2.33	11.51 = 101.30

PAYTINE, $C^{21}H^{20}N^2O.H^2O$, See CINCHONA-BASES (p. 497).

PECTEN. The muscular tissue of *Pecten irradians*, a mollusc found on the eastern coasts of the United States of America, and much prized as an article of food, has been found by N. H. Chittenden (*Sill. Am. J.* [3], x. 26) to contain considerable quantities of glycogen and glycocine. An analysis of the eatable portion gave:

	I	II
Water	79.60	80.25 p. c.
Solid parts	20.40	19.75
Ash	1.28	1.24
Nitrogenous Substance	15.68	15.04
Fat	0.33	0.32
Non-nitrogenous Substance	3.13	3.15

PECTOUS SUBSTANCES. E. Reichardt (*Arch. Pharm.* [3], x. 116) from a comparison of the earlier researches on the bodies of this group (iv. 363–370) infers that their composition differs but very slightly from that of the carbohydrates, and that the differences shown in some cases by the analyses may be attributed to impurities. Referring also to Scheibler's investigations on arabin and arabinose, and his own on pararabin (p. 119), he concludes that it is not advisable to place these bodies in a distinct group, but that they should be regarded as gelatinising carbohydrates, nearly related to the gums.

M. Giraud, on the other hand (*Compt. rend.* lxxx. 477), divides the mucilaginous or gummy substances of the vegetable kingdom into three groups: to the first of which belongs gum tragacanth, which is characterised by the presence of a body capable of yielding pectous substances; to the second, those which contain no pectous substances, and are rendered insoluble in water even by very dilute acids: an example of these bodies is afforded by quince-mucilage; and to the third group, those kinds of gum which are free from pectin, are not precipitated by dilute acids, but when heated therewith are converted into dextrin and sugar. All these substances are converted by heating with dilute acids into a crystallisable, non-fermentable sugar, which, therefore, is different from glucose. Gum tragacanth dissolves very slowly in cold water, but when treated with boiling water for twenty-four hours becomes perfectly

soluble and is converted into pectin. Gum-tragacanth, digested on the water-bath for three hours with acid of 1 per cent., is partly ($\frac{7}{10}$) converted into sugar, the greater portion, however, being converted into pectin. It therefore contains more than half its weight of a pectous substance, probably Frémy's pectose. By treating gum-tragacanth with 1 per cent. hydrochloric acid, precipitating with baryta, and decomposing the precipitate with hydrochloric acid, 60 per cent. of the weight of tragacanth employed is obtained as pectic acid, agreeing in its properties with that which Frémy prepared from fruits. A quantitative analysis of gum-tragacanth gave:

Water	20	p. c.
Pectous Substances	60	"
Soluble Gum	8 to 10	"
Cellulose	3	"
Starch	2 to 3	"
Mineral Substances	3	"
Nitrogenous Bodies	traces	

PELAGOSITE. G. Tschermak (*Jahrb. f. Min.* 1878, 751) examined numerous specimens of limestone and dolomite from the Mediterranean coast, which were covered with a grey, shining, varnish-like substance, formed where the waves act upon the rock. No organised structure was observed, but a chemical examination proved it to consist mostly of calcium carbonate. The finest specimens of this substance came from the island of Pelagosa, in the Adriatic; whence its name. Descloizeaux a. Vélain observed this peculiar incrustation on felspathic rocks in Corsica, on the coast of Oran, and on the basaltic lavas on the coast of Réunion.

PELAGONIC ACID, $C^6H^{17}.CO^2H$. This acid is found, together with its nitroso-derivative, $C^6H^{16}(NO)^2O^2$, amongst the products of the action of fuming nitric acid on *stearolic acid* (q.v.)

PELHAMINE. A black mass, resembling serpentine, occurring to the thickness of a foot in the asbestos mine of Pelham, Massachusetts; analysed by C. U. Shepard (*Sill. Am. J.* [3], xii. 231):

SiO ²	Al ² O ³	FeO	MgO	H ² O	Sp. gr.
38·40	2·80	15·52	39·88	3·40 = 100	2·9 to 3·2

PELLETIERINE. The alkaloïd of the pomegranate. To obtain it, the bark of the tree is roughly powdered and mixed with milk of lime to a thick paste, which is washed with water; the liquid is shaken with chloroform, which dissolves the pelletierine; the chloroform solution is then treated with a dilute acid; and the solution of a salt of the alkaloïd thus obtained is evaporated in a vacuum over sulphuric acid. To obtain the free base, the solution of one of its salts is treated with potassium carbonate and shaken with chloroform. The chloroform solution on evaporation leaves the alkaloïd as a colourless oily mass, boiling at about 180°, and very soluble in water, alcohol, or ether, and especially in chloroform. It has an alkaline reaction, and precipitates most of the metals from their salts. It is precipitated by barium chloride, the precipitate being soluble in excess of the reagent. A precipitate is also formed by bromine water in excess; by Nessler's reagent; by iodide of potassium and cadmium, and by phosphomolybdic acid. The sulphate, nitrate, and hydrochloride of pelletierine are crystalline and extremely hygroscopic (*Tanret, Compt. rend.* lxxxvi. 1270).

PENNINE. This mineral from the Zillerthal, where it occurs in transparent plates, sometimes uniaxial, sometimes biaxial, has been described by J. Rumpf. and analysed by van Warvecke (*Min. Mitth.* 1873, 33). P. Groth (*Zeitschr. Kryst.* i. 509) refers the greenish mass (regarded by Delesse as pyrosclerite) which often occurs, together with nuclei of felspar, in the granular limestone near Markirch in Alsace, to Kennigott's pseudophite (iv. 744), and regards this latter, together with a greenish steatitic mineral, occurring in the primitive limestone of Plaben near Bodweis, and of Ckyn in Bohemia, as dense varieties of pennine.

Analyses.—1. From the Zillerthal (van Warvecke). 2. Pseudophite from Moravia (v. Hauer, *Wien. Akad. Ber.* xvi. 170). 3. Greenish mineral from Plaben (v. Drasche, *Jahrb. f. Min.* 1873, 1204). 4. A similar mineral from Ckyn (Genth, *ibid.* 1874, 653).

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	CaO	H ² O
1.	34·24	12·62	1·64	3·35	34·86	0·30	14·14 = 101·15
2.	33·42	13·42	—	2·58	34·04	—	14·68 = 98·14
3.	34·63	17·13	—	1·61	33·38	—	13·93 = 100·68
4.	35·31	18·28	1·26	0·83	31·61	—	13·26 = 100·65

PENTABROMACETONE, C^6HBr^5O . When phlorobromin, C^6HBr^5O (a product of the action of bromine on phloroglucinol), is dissolved in warm alcohol, and the solution, after standing for several hours, is mixed with a large quantity of cold water, an oil is precipitated, together with slender needles, which, after being pressed and recrystallised from alcohol or chloroform, have the composition of pentabromacetone. The compound thus prepared melts at 76° , and is crystallographically identical with that which is obtained directly from acetone, forming orthorhombic prisms having the axial ratio $a : b : c = 0.6182 : 1 : 0.6928$, and exhibiting the faces $P, \infty P_2, \infty P_\infty$. Pentabromacetone is converted by ammonia, either aqueous or alcoholic, into dibromacetamide (Benedikt, *Liebig's Annalen*, cxxxix. 165).

PENTA-, TETRA-, and HEXBROMANTHRACENE. *Tetrabromanthracene* (vi. 178), exposed to the vapour of bromine for some days, is converted into *tetrabromanthracene tetrabromide*, $C^{14}H^4Br^4$, which crystallises from a hot saturated solution in carbon bisulphide in distinct, colourless prisms melting, with decomposition, at about 212° ; and this compound, heated to 230° till it ceases to give off bromine and hydrogen bromide, yields *pentabromanthracene*, $C^{14}H^3Br^5$, a pulverulent yellow substance which melts at 212° , dissolves sparingly in alcohol and ether, easily in benzene, toluene, and carbon sulphide, and is converted by oxidation with chromic acid into *tribromanthraquinone*, a body subliming in broad needles and melting at 365° .

Hexbromanthracene, $C^{14}H^2Br^6$, is formed, with violent reaction, when tetrabromanthracene tetrabromide is heated with alcoholic soda. It is but sparingly soluble in all solvents, and crystallises from petroleum (b. p. 130° – 160°) in golden-yellow silky needles, which may be sublimed, but do not melt even at 370° . By oxidation with chromic acid it is converted into *tetrabromanthraquinone*, $C^{14}H^4Br^4O^2$, which may be purified and crystallised in small needles from solution in carbon sulphide, but separates from all other solvents in the form of powder (Hammerschlag, *Ber.* x. 1212).

PENTABROMAZONAPHTHALENE. See AZONAPHTHALENE, under NAPHTHALENE.

PENTACETYL-GALACTOSE, $C^6H^7(C^2H^3O)^5O^5$. See GALACTOSE, under SUGARS.

PENTACETYL-SULPHOTANNIC ACID, $C^{12}H^4(C^2H^3O^2)^5(SO^3H)SO^2$. See TANNIC ACIDS.

PENTACHLOROBUTYLENE, $C^4H^3Cl^5$, is formed, together with other chlorinated compounds, by the action of chlorine on tertiary butyl alcohol (p. 360).

PENTACHLORONAPHTHALENE. See NAPHTHALENE.

PENTAMETHYLETHOL, or *Dimethyl - katabutyl Carbinol*, $C(CH^3)^3.C(CH^3)^2OH$. See HEPTYL ALCOHOLS (p. 1026).

PENTANES, C^5H^{12} . *Boiling Points.*—Normal pentane, $CH^3.(CH^2)^3.CH^3$, boils at 38° , isopentane, $CH^3.CH^2.CH(CH^3)^2$, at 30° , tetramethyl-ethane, $C(CH^3)^4$ at 9.5° (A. Naumann, *Ber.* vii. 173).

Isopentane (amyl hydride) in aqueous solution (1 c.c. to 2 litres of water) mixed with half its volume of chromic acid mixture (500 pts. water, 5 crystallised chromic anhydride, and 1 potassium dichromate) and left for five weeks at a temperature of 15° – 20° , was found to be converted into valeric acid (Berthelot, *Compt. rend.* lxxix. 1435).

Pentane from petroleum, and inactive isopentyl chloride, are converted by *chromyl chloride*, CrO^2Cl^2 , into chlormethyl-isopropyl ketone, $CH^2Cl.CO.CH(CH^3)^2$ (Etard; see KETONES, p. 1148).

PENTAPHENYLCHLORETHANE, $C(C^6H^5)^3.CCl(C^6H^5)^2$, is formed, together with diphenyl, by the action of monobromobenzene on carbon tetrachloride, the two substances being dissolved in ether, and sodium introduced into the solution, and may be extracted from the crude product by distilling off the ether and boiling the residue with alcohol. It melts between 120° and 125° , boils above 340° , and yields a nitro-derivative when treated with nitric acid (Guareschi, *Gazz. chim. ital.* 1877, 409).

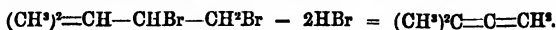
PENTATHIONIC ACID. See SULPHUR, OXYGEN-ACIDS OF.

PENTIC ACID, $3C^3H^4O^2 + H^2O$, and **PENTENIC ACID**, $3C^3H^4O^2 + H^2O$. The compounds so-called by Demarcay (not true acids) are formed by the action of 1 and 2 mol. bromine respectively on 1 mol. ethylic ethylacetoacetate, in the same manner as the homologous compounds hexic and hexenic acids are formed from ethylic acetovalerate (p. 1501). Ethylic methylacetoacetate, treated with bromine in like

manner, yields tetric acid, $3\text{C}^4\text{H}^4\text{O}^2 + \text{H}^2\text{O}$, and tetronic acid, $3\text{C}^4\text{H}^4\text{O}^3 + \text{H}^2\text{O}$. Tetric acid, m. p. 150° , and pentic acid, m. p. 189° – 190° , crystallise readily, and their aqueous solutions are reddened by ferric chloride. The reaction, indeed, appears to be general for compounds of this series (Demarçay, *Bull. Soc. Chim.* [2], xxvii. 483).

PENTINE, C^5H^8 . *Valerylene*.—This hydrocarbon is known in three modifications, viz.:

(1). $(\text{CH}^3)^2\text{C}=\text{C}=\text{CH}^2$. This is the compound which Reboul obtained by heating amylene bromide with alcoholic potash (v. 981):



It has a sp. gr. of 0.700 ; boils at 45° ; does not form compounds with silver or copper.

(2). *Propyl-acetylene*, $\text{CH}^3.\text{CH}^2.\text{CH}^2.\text{C}\equiv\text{CH}$, is formed in like manner by abstraction of 2HCl from propyl-methyl ketonic chloride, $\text{C}^3\text{H}^7.\text{CCl}^2.\text{CH}^3$. It boils at 50° , and yields metallic derivatives with silver and copper (Friedel).

(3). *Isopropyl-acetylene*, $(\text{CH}^3)^2\text{CH}.\text{C}\equiv\text{CH}$. Produced: α . By converting valeraldehyde, $(\text{CH}^3)^2\text{CH}.\text{CH}^2.\text{CHO}$, into the corresponding chloride, $(\text{CH}^3)^2\text{CH}.\text{CH}^2.\text{CHCl}^2$, by means of phosphorus pentachloride, and removing 2HCl from this chloride by the action of potash (Bruylants, *Ber.* vii. 759). β . By the action of alcoholic potash on the chloride of isopropylethylene, $(\text{CH}^3)^2\text{CH}.\text{CHCl}.\text{CH}^2\text{Cl}$ (Eltekoff, *Ber.* x. 707). It boils at 35° ; gives with ammoniacal copper solution a yellow precipitate; with ammoniacal silver solution, on heating, an amorphous white precipitate, which is lighter than water and is but little affected by light. When treated with a solution of iodine in potassium iodide, it takes up 2 at. iodine, and is converted into isopropyl-acetylene di-iodide, $(\text{CH}^3)^2\text{CH}.\text{CI}=\text{CHI}$, which boils without decomposition at 140° , is but very slightly affected by light, and is reconverted by sodium ethylate into isopropylacetylene. Sodium dissolves in isopropylacetylene, with evolution of hydrogen and formation of a compound which crystallises in large plates, but falls to powder in contact with the air, and is reconverted by water into isopropylacetylene (Eltekoff).

PENTIOIC ACIDS, $\text{C}^5\text{H}^{10}\text{O}^2 = \text{C}^5\text{H}^8.\text{COOH}$. 1. **Normal Pentoic Acid, $\text{CH}^3.(\text{CH}^2)^3.\text{COOH}$.** This acid, which Lieben a. Rossi obtained by oxidation of normal pentyl alcohol (vii. 1197), is also produced by heating normal hexoic (caproic) acid, $\text{CH}^3.(\text{CH}^2)^4.\text{CO}^2\text{H}$, in a water-bath with 1 mol. bromine, whereby it is converted into α -bromocaproic acid, $\text{CH}^3.(\text{CH}^2)^3.\text{CHBr}.\text{CO}^2\text{H}$; then adding sodium carbonate to permanent alkaline reaction; decomposing with sulphuric acid; dissolving out the resulting α -hydroxycaproic or normal leucic acid, $\text{CH}^3.(\text{CH}^2)^3.\text{CHOH}.\text{CO}^2\text{H}$, with ether; then expelling the ether, oxidising with chromic acid mixture, $[\text{C}^5\text{H}^{10}\text{O}^3 + \text{O}^2 = \text{C}^5\text{H}^{10}\text{O}^2 + \text{CO}^2 + \text{H}^2\text{O}]$, and distilling. The volatile acid contained in the distillate exhibits all the properties of the normal pentoic acid described by Lieben a. Rossi (Erlenmeyer, *Ber.* ix. 1840).

Normal Ethyl Pentoate, $\text{CH}^3.(\text{CH}^2)^3.\text{COOC}^2\text{H}^5$, boils, under a pressure of 736.5 mm. reduced to 0° , at 114.6° (corr.) Its sp. gr., referred to water at equal temperatures, is 0.894 at 0° , 0.8765 at 20° , and 0.8616 at 40° (Lieben a. Rossi, *Liebig's Annalen*, clxv. 117).

2. **Isopentoic, Isopropyl-acetic, Isobutyl-formic, Valeric, or Valerianic Acid, $(\text{CH}^3)^2\text{CH}.\text{CH}^2.\text{COOH}$.** This acid has been found by O. Jacobsen in geranium-oil (*Liebig's Annalen*, clvii. 232).

Preparation.—According to O. Ficin (Arch. Pharm. [3], iii. 219), dilute valeric acid may be formed by a continuous oxidation-process similar to that adopted for vinegar making (i. 8), the acidifier being filled with chopped valerian-root, and dilute fusel-oil repeatedly passed through it, the temperature being kept between 30° and 40° . The process, however, is mentioned as being merely of scientific interest, and not advantageous in practice. On the formation of valeric acid by oxidation of paraffin, see p. 1489.

For the preparation of pure valeric acid, H. Lescœur (*Bull. Soc. Chim.* [2], xxvii. 104) takes advantage of its property to form acid salts with potash and soda. A molecule of the neutral salt is mixed with 2 mol. of valeric acid; the acid salt is left to crystallise in the cold; the crystals are dried; and the acid separated from them by distillation. The pure acid begins to pass over a little above 200° , and the distillation should be stopped when the temperature rises to 300° .

According to Balbiano (*Gazz. chim. ital.* 1876, 229, 402), valeric acid, prepared from inactive amyl alcohol, boils at 174.1° under a pressure of 724 mm. (compare Erlenmeyer a. Hell, vii. 1199).

According to C. Schacht (*Arch. Pharm.* [3], ii. 97), *bismuth valerate* has the composition $\text{C}^5\text{H}^{10}\text{Bi}^4\text{O}^8 = (\text{C}^5\text{H}^8\text{O}^2)^4.\text{Bi}^4(\text{OH})^4\text{O}^4$.

On the *sp. gr.* of valeric acid and its ethers at different temperatures, see Pierre a. Puchot (vii. 1200).

Ethylic Acetovalerate, $C^6H^{10}O^2 = CH^3.CO.CH(C^2H^7).CO.OC^2H^5$ (Demarçay, *Compt. rend.* lxxxiii. 449; *Bull. Soc. Chim.* [2], xxvii. 483). This acid is formed by the action of isopropyl iodide on ethylic acetosodacetate:



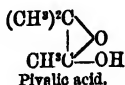
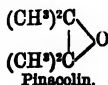
It boils at $200^\circ-202^\circ$ under a pressure of 758 mm.; colours ferric chloride pale violet. Bromine acts strongly on it; the action requires to be moderated by cooling. On adding 1 mol. bromine to 1 mol. of the ether, treating the oily product with alcoholic potash, and then adding hydrochloric acid, a body separates, which appears under the microscope to consist of elongated rectangular plates, and has the composition $3C^6H^{10}O^2 + H^2O$. This compound, called by Demarçay hexic acid, melts at $123^\circ-124^\circ$, boils with slight decomposition at about 263° , is slightly soluble in cold, moderately soluble in boiling water, easily in alcohol, ether, and chloroform, and separates from the ethereal solution in crystals several centimeters long. It is not a true acid, as it does not form salts, and the product obtained by treating it with phosphorus pentachloride is not decomposed by water.

1 mol. acetovaleric ether and 2 mols. bromine yield the compound $3C^6H^{10}O^2 + H^2O$, called hexenic acid, which is difficult to purify, melts at 187° , and boils with decomposition at $270^\circ-280^\circ$, yielding an oily distillate reconvertible by water into the original compound. The so-called hexenic acid is sparingly soluble in cold, freely in boiling water, also in alcohol and ether, very slightly soluble in chloroform.

Methyl-ethylacetic Acid, $(CH^3)(C^2H^5)CH.COOH$. The preparation of the ethylic ether of this acid by distilling ethylic methyl-ethylacetoacetate with sodium ethyl has already been described (p. 15). The acid obtained from it boils at 173° , and resembles ordinary optically active valeric acid in every respect excepting that it forms an amorphous barium salt (Saur, *Ber.* vii. 1037).

Trimethylacetic Acid, $(CH^3)^3C.COOH$, also called *Pivalic Acid*. This acid, which Butlerow obtained by saponification of katabutyl cyanide, $(CH^3)^3C.CN$ (vii. 1182), is also produced by oxidation of methyl-katabutyl ketone (pinacolin), $(CH^3)^3C.CO.CH^3$ (p. 1148), with chromic acid mixture (Friedel a. Silva, *Compt. rend.* lxxvii. 48). When separated from its sodium salt by sulphuric acid, it forms a crystalline mass which gradually becomes granular. The crystals belong to the regular system, as they do not exhibit double refraction. The acid dissolves in 46 pts. of water at 20° . It melts, according to Butlerow, at $34^\circ-35^\circ$; according to Friedel a. Silva at 30° after repeated partial fusion. It is separated from its salts even by acetic acid. The *potassium salt* is deliquescent. The *sodium salt*, $C^3H^7O^2Na + 2H^2O$, gives off its water of crystallisation on exposure to dry air, and, as well as the potassium salt, forms after fusion a laminar mass like the acetates (Friedel a. Silva); according to Butlerow, the sodium salt crystallises in flat prisms, very soluble in alcohol. The *barium salt*, $(C^3H^7O^2)^2Ba + 5H^2O$, and the *calcium salt*, $(C^3H^7O^2)^2Ca + 4H^2O$, form silky very soluble needles. The *silver salt* is obtained by precipitation in small laminae. The *copper salt*, $(C^3H^7O^2)^2Cu + H^2O$, is obtained by decomposing a soluble trimethylacetate with copper sulphate, as a heavy crystalline green precipitate, requiring more than 500 pts. water to dissolve it. The solution when evaporated leaves blue scales, consisting of a basic salt, which is also obtained by prolonged washing of the normal salt. The latter is obtained in the state of greatest purity by the action of free trimethylacetic acid on cupric carbonate. It gives off its water in a vacuum at ordinary temperatures. It may be freed from basic salt by solution in alcohol of 95 per cent., from which it crystallises in dark bluish-green prisms apparently having the composition $(C^3H^7O^2)Cu + H^2O + \frac{1}{2}C^3H^7O$; it is likewise soluble in ether. It sublimes when heated (Friedel a. Silva). The *zinc salt* is a white crystalline powder, unctuous to the touch, slightly soluble in water (Butlerow).

Friedel a. Silva resaponify pinacolin and its product of oxidation (pivalic acid) by the following formulæ:



But pinacolin being formed by the action of zinc-methyl on trimethyl-acetyl chloride, has much more probably the constitution of methyl-katabutyl ketone assigned to it by Butlerow (p. 1148), and may therefore be expected to be converted by oxidation into trimethyl-acetic acid. And, in fact, the only important difference between Butlerow's acid and the pivalic acid of Friedel a. Silva consists in the lower melting

point of the latter, which, as they observe, may have been due to a slight admixture of acetic acid, inasmuch as the lowest melting fractions yielded a silver salt, the percentage of silver in which was somewhat too high for the formula $C^5H^9O^2Ag$.

PENTOIC ALDEHYDE, $C^5H^{10}O$. See VALERAL.

PENTYL ALCOHOLS, $C^5H^{12}O = C^5H^{11}.OH$. These compounds have hitherto been described as *amyl alcohols* (i. 203; vi. 106–114; vii. 62; viii. 75–78); but it is better to designate them generally as *pentyl alcohols*, a term which indicates their place in the series of alcohols $C^nH^{2n+1}OH$, and restrict the term *amyl alcohol* to the one which has long been known by that name, viz., isopentyl carbinol, $(CH^3)^2CH.CH^2.CH^2OH$, the first discovered of the group. The following are the most recent additions to our knowledge of these bodies.

According to Wischnegradsky (*Liebig's Annalen*, exc. 328), the *amyl alcohol* of fermentation is a mixture of isopentyl alcohol (isobutyl-carbinol) with small quantities of normal pentyl alcohol and methyl-ethyl carbinol, which he regards as the optically active constituent.

The following dextrorotatory amylic ethers have been prepared by J. A. le Bel (*Bull. Soc. Chim.* [2], xxi. 542) from levorotatory *amyl alcohol*:

Chloride.	B.-p. 97°–99°	$[\alpha]_D = +1.24$
Bromide.	„ 117°–120°	$[\alpha]_D = +3.75$
Iodide.	„ 144°–145°	$[\alpha]_D = +5.34$ to 5.12

Methyl-amyl and amylene from active *amyl alcohol* are inactive.

Methyl-isopropyl Carbinol, $CH^3.CHOH.CH(CH^3)^2$ (Winogradoff, *Liebig's Annalen*, exci. 125). This secondary alcohol is formed by acting on zinc-methyl with bromoacetyl-bromide, and treating the product with water. To avoid explosions, it is best to pour the acid bromide (1 mol.) into the zinc-methyl (3 mols.) through a tap-funnel, the neck of which dips into the liquid. The mixture, after being left to itself for some weeks, is mixed with water and hydrochloric acid and distilled; and the chief product (50 per cent. of the theoretical quantity) which passes over between 110° and 120°, is treated first with anhydrous baryta, and then with sodium, in order to remove the last portions of water and bromine.

On the mechanism of the reaction, see the original paper, and *Chem. Soc. J.* xxiv. 485.

Methyl-isopropyl carbinol thus obtained is a liquid having a faint odour, easily soluble in water, boiling at 113°, and not solidifying at -33° . Its specific gravity is 0.8308 at 0°, and 0.8219 at 19°. With bromine it yields an amylene. By phosphorus pentachloride, and by gaseous hydrogen iodide with aid of heat, it is converted into tertiary pentyl chloride and iodide (*infra*).

Dimethyl-ethyl Carbinol, $(CH^3)^2(C^2H^5)COH$. In the preparation of this tertiary alcohol by distilling 5 grams of commercial amylene with sulphuric acid (2 vols. H^2SO^4 to 1 vol. water), Butlerow (*Ber.* x. 81) obtained two grams of the pure alcohol (comp. p. 81). It melts at -12° , and boils at 102°–104°. The corresponding chloride boils at 86°, the bromide between 108° and 109°, the iodide between 127° and 128° (*Wischnegradsky, Liebig's Annalen*, exc. 331).

PENTYL-GLYCOLS or PENTYLENE ALCOHOLS. Three of these compounds are known, and have been already described (i. 208, and pp. 81 and 82 of this volume), viz.:

Trimethyl glycol, $(CH^3)^3COH.CHOH.CH^3$	B.-p. 177°
Methyl-ethyl glycol, $(C^2H^5).CHOH.CHOH.CH^3$	187.5°
Isopropethylene glycol, $CH(CH^3)^2.CHOH.CH^2OH$	206°

PENTYLENES, C^5H^{10} . *Amylenes*.—Three of these hydrocarbons have already been described (p. 79), viz.:

Isopropylethylene, $H^2C=CH[CH(CH^3)^2]$.
 Methyl-ethyl-ethylene, $H^2C=C(CH^3)(C^2H^5)$.
 Trimethyl-ethylene, $(CH^3)^3C=CH(CH^3)$.

(1). According to Wischnegradsky (*Ber.* x. 81; *Liebig's Annalen*, exc. 328), Flavitzky's amylene, boiling at 25°, is a mixture of two isomeric hydrocarbons: for when the iodide obtained from ordinary *amyl alcohol* (rot. power = $+2.9^\circ$) is treated with alcoholic potash, a hydrocarbon is formed, having a variable boiling point (23°–27°), and from this, on agitation with sulphuric acid, a third hydrocarbon is dissolved, while an amylene boiling at 21°–22° (regarded by Wischnegradsky as *isopropylethylene*) remains behind. The same hydrocarbon (boiling at 21.5°–22°, and behaving similarly with sulphuric acid) is also formed from the comparatively inactive

amyl iodide (rot. power = + 0.3 (which is obtained, together with ethyl iodide, by the action of hydriodic acid on amyl-ethyl oxide). (2). Ordinary (commercial) amylene, obtained by the action of zinc chloride on ordinary amyl alcohol, appears to contain three pentylenes, viz., trimethyl-ethylene, unsymmetrical methyl-ethyl-ethylene, $\text{H}^2\text{C}=\text{C}(\text{CH}^3)(\text{C}^2\text{H}^5)$, and normal propyl-ethylene. The pentylene prepared from ordinary amyl chloride contains two isomerides, viz., unsymmetrical methyl-ethylene and isopropyl-ethylene.

The presence of isopropyl-ethylene in the amylene boiling at 25° is further confirmed by the experiments of Eltekoff (*Ber.* x. 707), from which it appears that the bromide of this amylene, when treated with alcoholic potash, yields, together with ethyl-valeryl oxide (b.-p. 111° – 114°), a pentine or valerylene, C^5H^8 , having the constitution of *isopropyl-acetylene*, $\text{HC}\equiv\text{C}-\text{CH}(\text{CH}^3)^2$ (p. 1500).

Oxidation.—The products obtained by the action of various oxidising agents on amylene have been examined by F. Zeidler (*Liebig's Annalen*, clxxxvi. 245). (1). *Amylene*, b.-p. 35° (from optically active amyl alcohol, with stannic chloride), yielded with potassium permanganate in neutral or alkaline solution: carbonic, formic, acetic, and succinic acid; with permanganate in sulphuric acid solution: carbonic, butyric, propionic, acetic, oxalic acids; with potassium dichromate and sulphuric acid: carbonic, butyric, acetic, and propionic acids; with chromic acid: carbonic acid, acetic acid, a higher fatty acid, and succinic acid; with potassium iodate in acid solution: carbonic and acetic acid. (2). *Amylene*, b.-p. 22° – 23° (from the hydriodic ether of optically active amyl alcohol with alcoholic soda), yielded with potassium permanganate in neutral or alkaline solution: carbonic, acetic, butyric, propionic (?), oxalic, and succinic acids; in acid solution: carbonic, acetic, higher fatty acids, a small quantity of succinic and a large quantity of oxalic acid; with potassium dichromate and sulphuric acid, or with chromic acid: carbonic, acetic, propionic, and butyric acids; with potassium iodate: carbonic and acetic acids; with nitric acid: carbonic acid, acetic acid, and a nitro-derivative. (3). *Amylene*, b.-p. 33° , from ethyl-amyl oxide with phosphoric anhydride, yielded with potassium permanganate in neutral acid or alkaline solution: carbonic, acetic, and oxalic acids; with potassium dichromate and sulphuric acid or with chromic acid: carbonic, acetic, and propionic acids; with potassium iodate or nitric acid: carbonic and acetic acids.

PEPPER. The amounts of moisture, ash, and nitrates (reckoned as nitric acid), also of alcoholic and aqueous extract in the kinds of pepper most frequently met with in commerce, have been determined by A. Wynter Blyth (*Chem. News*, xxxii. 140) with the following results:

	Moisture	Soluble ash	Total ash	Nitric acid	Alcoholic extract	Aqueous extract
Penang	9.531	2.212	4.189	0.0447	7.650	18.335 p.c.
Tellicherry . . .	12.908	3.380	5.770	0.0886	7.896	16.500 "
Sumatra	10.103	2.626	4.316	0.0656	6.450	17.500 "
Malabar	10.548	3.453	5.195	0.0386	6.375	20.375 "
Trang	11.664	2.538	4.775	0.1187	6.300	18.175 "

The ash of Tellicherry pepper was found to have the following composition:

K ² O	Na ² O	MgO	CaO	Fe	P ² O ⁵	SO ²	Cl	CO ²	Sand
24.38	3.23	13.00	11.60	0.30	8.47	9.61	7.57	14.00	6.53 = 98.69

H. Pocklington (*Pharm. J. Trans.* [3], v. 681) found in three sorts of commercial pepper from 50 to 60 per cent. of foreign substances, consisting of arrow-root, rice-starch, wheat-flour, pea-flour, and oatmeal.

On the adulterations of pepper, see also Landrin (*Monit. Scient.* vi. 883).

PEPPERMINT OIL. According to J. Moss (*Pharm. J. Trans.* [3], v. 566), Japanese peppermint-oil begins to boil at 206° , the temperature then remaining constant for some time, and ultimately rising to 218° . The oil did not deposit any crystals when cooled. The camphor or stearoptene of Japanese peppermint-oil melts at 30° , resolidifies at 37.5° , and boils at 215° ; compare Oppenheim (iii. 880). According to J. Mackay (*Pharm. J. Trans.* [3], v. 825), 1 pt. of the Japanese oil dissolves readily at ordinary temperatures in 8 pts. of rectified spirit. The liquid oil easily dissolves the camphor, and deposits it in crystals when cooled. Peppermint-camphor distilled with zinc chloride yields menthene, $\text{C}^{10}\text{H}^{18}$ (Beckett a. Wright, p. 1274).

According to C. Jehn (*Arch. Pharm.* [3], iii. 29), peppermint-oil in contact with

chloral hydrate gradually assumes a dark cherry-red colour, which is easily transferred to ether, alcohol, and chloroform, is not destroyed by boiling, but becomes darker on addition of a small quantity of sulphuric acid; and on subsequent addition of chloroform, acquires a shade more inclining to dark violet. This reaction is not exhibited by other volatile oils. Danin von Wassowicz (*ibid.* xi. 510) has examined the action of chloral hydrate on seven varieties of peppermint-oil, viz.: 1. French; 2. English (Mitcham); 3. American; 4. German; 5. From *Mentha piperita*, cultivated in Galicia; 6. An older English sample diluted with an equal volume of alcohol; 7. A viscid, dark-yellow American oil. 1, 2, 5, 6, and 7 exhibited no coloration after five minutes; 3 after the same time was coloured light violet; 4, yellowish-brown. After the lapse of an hour, only 2, 5, and 6 remained uncoloured. When heated, all the varieties became coloured, and coloration was likewise immediately produced, when an impure chloral hydrate containing hydrochloric acid was used as the reagent.

According to E. B. Shuttleworth (*Diagl. pol. J.* cccviii. 464; *Amer. J. Pharm.* 1872, xlv. 171), American peppermint-oil is sometimes adulterated with alcohol and castor oil.

According to M. A. Frebault (*Pharm. J. Trans.* [3], iv. 977), peppermint-oil treated with picric, sulphuric, hydrochloric, or nitric acid, especially the first, yields a green substance which exhibits red fluorescence, and agrees in many of its reactions with chlorophyll.

PEPSIN. E. Scheffer (*Pharm. J. Trans.* [3], ii. 761, 783, 843) prepares pepsin by macerating the mucous membrane of pigs' stomachs for several days with water containing hydrochloric acid, and mixing the liquid, after it has been strained and left to clarify for 24 hours, with an equal volume of a saturated solution of common salt; the pepsin which rises to the surface is skimmed off after a few hours, then pressed and dried without application of heat. The stiff, hard, straw- to brown-yellow substance thus obtained contains a certain quantity of mucus and small quantities of calcium phosphate and sodium chloride, which however do not interfere with its action. Sweetened pepsin is prepared by mixing recently pressed pepsin with pulverised milk-sugar, and drying the mixture by exposure to the air. The milk-sugar by its antiseptic properties may perhaps conduce to the preservation of the pepsin. The aqueous solution of pepsin quickly decomposes. The digestive power of pepsin may be tested by noting the time required for dissolution, under its influence, of a given quantity of coagulated white of egg at a given temperature. The last portions of albumin require for their disappearance a proportionately longer time, even when the pepsin is present in excess. 1 grain of purified pepsin in 4 ounces of salt water dissolved 400 grains of albumin in 18 hours at 24°.

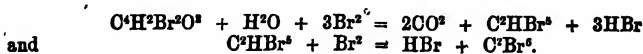
According to H. Sellon (*Pharm. J. Trans.* [3], iv. 89), the yield of pepsin by Scheffer's method is considerably increased if the digestion of the mucous membrane with dilute hydrochloric acid be performed at 37°. Scheffer's pepsin is contaminated with syntonin, and perhaps also with other proteids. Durable preparations may be obtained by trituration with milk-sugar or solution in glycerin.

Various kinds of pepsin are described by E. Rennard (*Russ. Zeitschr. Pharm.* 1874, 577; *Jahresb. f. Chem.* 1874, 944).

Volumetric Estimation.—Pepsin may be estimated volumetrically by means of fibrin which has been coloured through and through with an ammoniacal solution of carmine. This coloured fibrin may be preserved in glycerin, and when required for experiment, must be carefully freed from glycerin by rinsing with water, cut up with scissors, and drenched with a five-fold quantity of hydrochloric acid. In this manner a crimson, translucent, gelatinous mass is obtained, which must be divided into portions of equal size, best on bibulous paper, which absorbs the excess of acid. On drenching these separate portions of coloured fibrin with pepsin-solutions of various strength, red liquids are obtained, the coloration being deeper and quicker as the pepsin-solution is stronger, so that it is easy to distinguish strong from weak solutions of pepsin, and possible to apply the method for quantitative estimation (P. Grützner, *Zeitschr. anal. Chem.* 1874, 106).

PEPTONES. See PROTEIDS.

PERBROMETHANE or **HEXBROMETHANE**, C^2Br^6 , is formed, together with other products, by heating mucobromic acid (vii. 828) with bromine and water to 120°–130° in sealed tubes:



It crystallises from carbon sulphide in thick colourless prisms, which are insoluble in alcohol and decompose at 200°–210° (Delbrück, *Liebig's Annalen*, clxv. 253).

PERBROMIC ACID, BrHO^4 . Muir in 1874 described the formation of this acid by agitating bromine with aqueous perchloric acid (p. 351). Subsequent experiments however failed to yield the same result, so that the conditions under which the formation of this acid takes place cannot yet be considered as satisfactorily established (Muir, *Chem. Soc. J.* 1876, xxx. 469). The formation of perbromic acid by the action of bromine on perchloric acid was previously announced by Kämmerer in 1863 (iv. 374); his results have however been called in question by R. W. E. Macivor (*Chem. News*, xxxiii. 35).

PERBROMOBENZENE, C^6Br^6 . On the formation of this compound from benzene, and on its properties, see BENZENE-DERIVATIVES (p. 170). According to E. Wall (*Ber.* ix. 1649), bodies of the fatty series, when subjected to exhaustive bromination with iodised bromine, yield in the first instance perbromomethane, which by prolonged heating to its boiling point, or to 300° in a sealed tube, is converted into perbromobenzene.

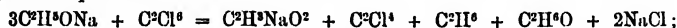
PERBROMOMETHYLMERCAPTAN, $\text{CSBr}^4 = \text{CBr}^2\text{SBr}$, is formed in small quantity when carbon disulphide mixed with bromine and a little iodine is left under water for a few minutes, and remains after the carbon sulphide and bromine have been distilled off on the water-bath, as a yellowish liquid, which smells like perchloromethylmercaptan (*infra*), distils at 150° , and acts on potassium sulphite even more violently than the chlorine-compound, forming methylmercaptantrisulphonate and bromide of potassium (Rathke, *Liebig's Annalen*, clxvii. 195).

PERBROMOPHENOL, $\text{C}^6\text{Br}^5\text{OH}$ (m. p. 225°), formed from phenol by the action of iodised bromine, is converted by heating with PBr^3 into perbromobenzene (Gessner, *Ber.* ix. 1505; Ruoff, *ibid.* x. 1234).

PERCHLORETHANE, $\text{Cl}^4\text{C.CCl}^3$. This body is formed: α . Together with perchloromethane, by heating propane or propyl chloride (b. p. 46.5°) with iodine chloride to 100° – 200° in a sealed tube, which is frequently opened to allow the resulting hydrogen chloride to escape, and then filled with chlorine gas (Krafft a. Merz, *Ber.* viii. 1296; see p. 1066). β . By the action of iodine trichloride on propionic acid: $\text{C}^2\text{H}^3.\text{CO}^2\text{H} + 4\text{ICl}^3 = \text{C}^2\text{Cl}^4 + \text{CO}^2 + 6\text{HCl} + 2\text{I}^2$ (Krafft, *Ber.* ix. 1085). γ . Together with perchlorobenzene, by exhaustive chlorination of diphenyl-trichlorethane, $(\text{C}^6\text{H}^5)^2\text{CH.Cl}^3$ (Ruoff, p. 1066). δ . Together with perchloromethane and perchlorobenzene, by heating chrysene with antimony pentachloride (Ruoff, *Ber.* x. 1234).

Perchlorethane melts at 179° (Geuther a. Brockhoff, *J. pr. Chem.* [2], vii. 108).

Reaction with Sodium Ethylate.—When perchlorethane (1 mol.), dissolved in ether, is heated with sodium ethylate free from alcohol (6 mol.) in a reflux apparatus, to the upper end of which is attached a glass tube dipping 250 cm. deep into mercury, a reaction commences at about 110° , after the greater part of the ether has distilled off, attended with evolution of a combustible gas; and afterwards a liquid distils over, consisting of alcohol, perchlorethylene, C^2Cl^4 , trichlorethoxyethylene, $\text{CCl}^2 = \text{CCl}(\text{OC}^2\text{H}^5)$, and triethyl dichloracetate, $\text{CHCl}^2.\text{C}(\text{OC}^2\text{H}^5)^2$, the last two products being due to the reaction between sodium ethylate and perchlorethylene (p. 754). The residue of the distillation contains unaltered sodium ethylate, sodium acetate, sodium ethylglyoxylate, $\text{CH}^3(\text{OC}^2\text{H}^5).\text{CO}^2\text{Na}$, a small quantity of sodium oxalate, and two resinous compounds, one of which separates on treatment with water, while the other is precipitated on addition of hydrochloric acid. In this reaction the perchlorethane probably first acts on the sodium ethylate, forming sodium acetate, perchlorethylene, and ethane, according to the equation:



and the perchlorethylene then acts further on the sodium ethylate in the manner above indicated (Geuther a. Brockhoff, *J. pr. Chem.* [2], vii. 101).

PERCHLORETHYLENE, C^2Cl^4 . *Carbon dichloride*.—This compound is formed, together with perchloromethane, by heating perchloropropane to 300° ; $\text{C}^3\text{Cl}^6 = \text{C}^2\text{Cl}^4 + \text{CCl}^3$ (Krafft a. Merz, *Ber.* viii. 1045). It may be prepared by heating perchlorethane, mixed with twice its weight of aniline to 170° (Bourgoin, p. 754).

On the reaction of perchlorethylene with sodium ethylate, and on perchlorethylene dibromide or dibromotetrachlorethane, see also p. 754.

PERCHLORIC ACID. According to T. Fairley (*Brit. Assoc. Reports*, 1874, 58), hypochlorous acid and its salts are converted into perchloric acid and perchlorates by passing ozonised air through their solutions.

On the Perchlorates of Potassium and Bismuth, see p. 450.

PERCHLOROBENZENE, C^6Cl^6 , is formed in the exhaustive chlorination of various hydrocarbons of the aromatic series with chlorine containing iodine (p. 1066);

also in the chlorination, by similar means, of secondary hexyl iodide (from mannite) (Krafft, *Ber.* ix. 1085); and, together with perchloromethane and perchlorethane, by heating chrysene with antimony pentachloride (Ruoff, *Ber.* x. 1234).

PERCHLORODIPHENYL, $C^{12}Cl^{10}$, is formed by exhaustive chlorination of diphenyl (Ruoff); also of diphenol, benzidine (diamidodiphenyl), and carbazol or diphenylimide, $NH(C^6H^4)^2$ (Zetter, *Ber.* x. 1233).

PERCHLOROMESOL. This name is given by Krafft to a chloride of carbon, C^4Cl^4 , which is commonly produced, together with the perchlorinated derivatives of methane, ethane, and benzene, in the perchlorination of fatty bodies. It is insoluble in water, but dissolves in alcohol, and crystallises therefrom in thin shining prisms, melting at 390° . It boils, with decomposition and evolution of chlorine, at 283° – 284° (mercury column wholly in the vapour; bar. 377 mm.)

PERCHLOROMETHANE, CCl^4 . *Carbon Tetrachloride*.—This compound is formed, together with carbon dioxide, by the action of iodine trichloride on trichloroacetic acid (Krafft, *Ber.* ix. 1085); also, together with perchlorethane or perchlorobenzene, or both, by the action of iodine trichloride or of chlorine and iodine on various hydrocarbons (p. 1066); and, together with perchlorethylene, C^2Cl^4 , by the decomposition of perchloropropane at 300° (p. 1505). The action of perchloromethane on sodium ethylate is not very definite, yielding merely two brown compounds together with sodium carbonate and a little oxalate.

PERCHLOROMETHYL-MERCAPTAN, $CCl^3S = CCl^3.SCl$, is formed, as already described (vii. 266), together with trichloromethylsulphurous chloride, by the action of dry chlorine on carbon disulphide. It is an oily liquid boiling at 147° (corr.), and having a sp. gr. of 1.712 at 12.8° (referred to water at 0°). Heated to 160° with zinc chloride, it deposits a considerable quantity of sulphur in crystals, and yields zinc chloride, perchloromethane, carbon disulphide, and a small quantity of thiocarbonyl chloride, $CSCl^2$. On potassium cyanide it acts violently, with great rise of temperature and carbonisation. It does not act on mercuric cyanide at ordinary temperatures, but when the mass was heated to 150° , it charred and burst the tubes.

PERCHLORONAPHTHALENE. See NAPHTHALENE (p. 1350).

PERCHLOROPROPANE, C^3Cl^8 , is obtained: 1. By heating trichlorhydrin, $C^3H^3Cl^3$, to 200° with iodine chloride (Krafft a. Merz, *Ber.* viii. 1045). 2. Together with perchloromethane by heating isobutane to 240° with iodine chloride, $C^4H^{10} + 11Cl^2 = C^3Cl^8 + CCl^4 + 10HCl$ (Krafft a. Merz, *loc. cit.*) 3. Together with perchlorethane and perchloromethane, by the action of iodine trichloride on isobutyric acid (Krafft, *ibid.* ix. 1076). Perchloropropane is resolved at 250° into perchlorethane and perchloromethane (Krafft a. Merz).

PERCHLOROTRIPHENYLAMINE, $(C^6Cl^5)^3N$. See PHENYLAMINES.

PEREIRO BARK. The bark of Pao Pereiro (*Geissospermum Vellozii*, Peckolt, & Leve, Baillon) also called *Pinguiciba* and *Canudo amargosa*, is employed in Brazil as a febrifuge. It contains at least two alkaloids which have been extracted by O. Hesse (*Ber.* x. 2162). One of these, called geissospermine, crystallises in small white prisms terminated by domes, dissolves very sparingly in water and in ether, easily in alcohol and in dilute acids, and is precipitated from the acid solutions by ammonia and caustic soda in white amorphous flocks which soon become crystalline. The hydrochloric acid solution forms with *platinic chloride* a pale yellow amorphous precipitate, with *auric chloride* a brown-yellow precipitate without reduction of metal. Geissospermine dissolves in strong nitric acid with purple-red colour, becoming yellow on heating; with strong sulphuric acid it forms a colourless solution gradually becoming pale yellow; sulphuric acid containing molybdic acid immediately dissolves it with blue colour. Crystallised geissospermine has the composition $C^{10}H^{14}N^4O^2.H^2O$, and gives off its water at 130° . Its *platinochloride* has the formula $(C^{10}H^{12}N^4O^2.HCl)^2 + PtCl^4$.

A second alkaloid of Pereiro bark, called *Pereirine*, is an amorphous powder easily soluble in alcohol, coloured blood-red by strong nitric acid, violet-red by pure sulphuric acid.

PERICLASE. This mineral from the Predazzite of Monte Somma, of which it forms from 9 to 41 per cent., has been analysed by A. Cossa (*Gazz. chim. ital.* 1877, 393) with the following results:

MgO	FeO	Sp. gr. = 3.642.
95.39	4.56 = 99.95	
95.78	4.13 = 99.91	

Cossa has prepared isotropic laminae of periclase by fusing magnesium sulphate with

sodium chloride in a platinum crucible for four hours, and leaving the fused mass to cool slowly. When a little ferrous sulphate was added, larger laminæ were formed containing 0.96 per cent. FeO.

PERIODIC ACID. See IODINE, OXYGEN ACIDS OF (p. 1095).

PERMANGANATES. On *Potassium Permanganate*, see p. 1267. On the rapid oxidation of Essential Oils and other Organic Substances by a mixture of this salt with strong sulphuric acid, see OILS (p. 1430).

Silver Permanganate is prepared by dissolving 158 pts. potassium permanganate with aid of heat, in 500 pts. water, and adding a solution of 170 pts. silver nitrate in 200 water, whereupon the silver permanganate separates in fine black, metallicallly lustrous crystals, half an inch long, which may be purified by recrystallisation from hot water, washing with cold water, and drying (Martenson, *Russ. Zeitschr. Pharm.* 1878, 66).

Zinc Permanganate is prepared for pharmaceutical purposes by dissolving 127 pts. of the silver salt just described in hot water, stirring in 68 pts. of zinc chloride made as neutral as possible (best prepared from zinc sulphate and barium chloride), and filtering the liquid through gun-cotton. The filtrate is then evaporated on the water-bath to a viscid consistence and left to cool, whereupon it solidifies to a crystalline mass. Zinc permanganate thus prepared is a black-brown metallicallly lustrous salt, very soluble in water, and deliquescing in damp air. When heated in a glass tube it gives off a purple vapour, and leaves a porous residue having the lustre of steel. When it is heated on platinum foil, the foil becomes coated with a ring-shaped deposit having a fine blue and yellow colour (Martenson, *loc. cit.*)

PEROWSKITE, $\text{CaO} \cdot \text{TiO}_2$. Hesseberg observed that this mineral, though belonging to the regular system, is bi-refractive, and attributed this anomaly to an internal transformation of the substance (vii. 899). The monometric character of the crystals has been confirmed by the measurements of N. v. Kokscharow (*Jahrb. f. Min.* 1876, 741; 1878, 88), and Des Cloizeaux (*ibid.* 749). According to v. Kokscharow, the mineral is optically biaxial, not uniaxial as stated by Hesseberg. Most of the Russian perowskites are not simple crystals, but penetration-twins. Des Cloizeaux, who has measured crystals of perowskite from Zermatt, attributes their optical characters to twin-formation and to the enclosure of bi-rofractive lamellæ of foreign substances.

A. Knop (*Jahrb. f. Min.* 1877, 647) finds that the mineral from the Kaiserstuhl range, hitherto described as perowskite, contains niobic as well as titanîc acid, and designates it as *dysanalite*. The following is the result of his analysis, after deduction of silica:

TiO_2	Nb_2O_5	Cerium oxides	CaO	FeO	MnO	Na_2O
41.47	23.23	5.72	19.77	5.81	0.43	3.57 = 100.

with traces of magnesia, potash, and fluorine, and small quantities of alumina. The sp. gr. of the mineral was found to be 4.13, which is perhaps too low; in consequence of the admixture of quartz and augite. The analysis leads to the formula $8\text{RTiO}_3 \cdot \text{RNb}_2\text{O}_6$, and shows that dysanalite is a titanoniobate intermediate between perowskite, which is a pure titanate, and koppite (p. 1158), which is a pure niobate.

PERPHENYL-MELAMINE, $\text{C}^{88}\text{H}^{80}\text{N}^6 = \text{C}^3(\text{C}^6\text{H}_5)^6\text{N}^6$, is formed by the action of cyanogen chloride on diphenylamine (p. 909).

PERSICIN. See PYRETHRUM.

PERTHIOCYANIC ACID, $\text{C}^2\text{H}^2\text{N}^2\text{S}^2$, according to R. W. Atkinson, $\text{C}^2\text{HN}^2\text{S}^2$, according to Ponomareff (p. 608). Ponomareff finds by further experiments (*Compt. rend.* lxxx. 1398) that perthiocyanic acid, heated with ammonia to a temperature not exceeding 100° (in his former experiments the heat was raised to 150° – 160°), yields a compound, $\text{C}^2\text{H}^2\text{N}^2\text{S}^2$, which he designates as thiammeline, together with thio-melanuronic acid, $\text{C}^2\text{H}^2\text{N}^2\text{S}^2$. Thiammeline is a white sandy powder which dissolves in 145 pts. of boiling water, and when heated with potash gives off ammonia and yields cyanate and thiocyanate of potassium. Hot strong hydrochloric acid resolves it into hydrogen sulphide, sal-ammoniac, and cyanuric acid. Nitric acid oxidises it to ammeline nitrate. Heated with ammonia, it yields a body having the properties of melamine. Thiammeline dissolves in acids and alkalis, and forms precipitates with the salts of the heavy metals.

Acetyl-perthiocyanic Acid, $\text{C}^2\text{H}(\text{C}^2\text{H}^2\text{O})\text{N}^2\text{S}^2$ (p. 609).

PERU BALSAM. According to Baillon (*Pharm. J. Trans.* [3], iv. 385), Peru and Tolu balsams are the produce of the same tree, and the differences between them arise merely from the modes of preparation (comp. BALSAMS, i. 496, 498).

For testing the purity of Peru balsam, the *Apothekerzeitung* recommends the determination of its specific gravity. The pure balsam has a sp. gr. of 1.14–1.16; mean 1.15. Peru balsam, which sinks in a solution of 1 pt. common salt in 5 pts. water (sp. gr. 1.125), may be regarded as pure (*Vierteljahrsschrift. pr. Pharm.* xxii. 99). Werner (*ibid.* 295) regards this method as inexact, and gives the preference to that which is recommended in the Pharmacopœia Germanica—namely, mixing the balsam with strong nitric acid and washing with water, pure balsam thus treated yielding a brittle mass, whereas adulterated balsam leaves an unctuous residue.

PETROCENE. This name is given by Hemilian (*Ber.* ix. 1604) to a hydrocarbon, $C^{22}H^{22}$, which may be separated from the highest-boiling portions of American petroleum. It crystallises from boiling benzene in yellow shining laminæ, is nearly insoluble in alcohol and ether, melts above 300° , sublimes when cautiously heated. By dilute nitric acid and chromic acid it is oxidised to a brown powder which is insoluble in the ordinary solvents, and sublimes with decomposition. With strong nitric acid and with bromine it yields substitution-products, and with sulphuric acid a sulphonic acid which forms insoluble lead and barium salts.

PETROLEUM. *Occurrence and Formation.*—O. Silvestri (*Gazz. chim. ital.* x. 1) found in the cavities of a prehistoric doleritic lava, 22 kilometers S.S.E. of the central cone of Etna, a petroleum-like substance, forming about 1 per cent. of the rock-mass, perfectly fluid at 20° , but hardening partially at 17° . The sp. gr. of the lava in its original state was 2.797; after the extraction of the petroleum by ether, 2.849. An analysis of the crude petroleum gave:

C	H	S	O
82.49	11.61	3.33	2.57 = 100.

Proximate analyses yielded:

	Per cent.
Light Hydrocarbons of sp. gr. 0.860 (at 24°) and boiling at 79° – 80°	0.74
Hydrocarbons of sp. gr. 0.925 to 0.9408 (at 24°) and boiling at 190° – 280°	17.23
Hydrocarbons of sp. gr. 0.946 to 0.9604 (at 24°) and boiling at 230° – 400°	31.95
Paraffin melting at 52°	19.90
" " 57.2°	22.89
Asphalt	2.90
Sulphur crystallising in monoclinic prisms	4.30
" " rhombic pyramids	0.09

The hydrocarbons were found to be paraffins, C^nH^{2n+2} , the value of n ranging from 13 to 18; their formation is attributed by Silvestri to the covering of organic structures by the liquid lava, the organic matter being thereby subjected to a kind of dry distillation, the products of which condensed in the already viscid upper portion of the lava-stream and made it porous.

The formation of petroleum beneath the earth's surface is also generally attributed to the decomposition of organic remains. Mendelejeff, however (*Ber.* x. 229), objects to this view, chiefly on the ground that mineral oils are found in tertiary strata in the Caucasus, and in Devonian and Silurian strata in Pennsylvania, and must have been formed in underlying and still older strata where but few organic remains could have existed. He supposes that, as a consequence of the condensation of the earth's substance from vapours, the interior must consist to a great extent of metals (iron predominating) in combination with carbon; and that water, acting on these carbides at high pressures and temperatures, produced metallic oxides and hydrocarbons, which latter, rising in the state of vapour, became condensed in the superincumbent strata, especially in porous sandstones.

Composition. Properties. Uses. American petroleum, as shown by the analyses of Pelouze a. Cahours (iv. 385), consists mainly of *paraffins*, C^nH^{2n+2} , from C^4H^{10} to $C^{15}H^{32}$. By fractional distillation, sometimes with the aid of steam, ordinary or superheated, and purification of the distillates with caustic potash, a number of commercial products are obtained which are applied to various purposes, the lighter oils chiefly as solvents for resins, &c., the heavier for burning in lamps and as fuel for steam-boilers. The following account of them is taken mainly from Dammer's 'Kurzes Handwörterbuch der Chemie':

Rhigolene, b. p. 30° , used as an anæsthetic.

Petroleum-ether (Kerosene, Rhigolene, Sherwood-oil): distils at 45° – 60° : clear, colourless oil having only a faint odour of petroleum; b. p. 50° – 60° ; sp. gr. 0.665; absorbs oxygen from the air and becomes heavier (0.670–0.675); extremely inflammable; used as a remedy for rheumatic pains and as a local anæsthetic.

Petroleum-ether, II. (Gasoline, Canadol): distillate between 60° and 70° ; has a sp. gr. of 0.665; second distillate between 70° and 90° .

Petroleum-benzin: distillate between 70° and 120° ; has a sp. gr. of 0.680 to 0.700; dissolves in alcohol and ether; boils at 60° – 80° ; absorbs oxygen and becomes heavier; dissolves fats, caoutchouc, asphalt, and turpentine; less easily colophony, mastic, and dammar resin; kills all small animal organisms, and is used externally as a remedy for itch and other skin diseases, internally for gastric pains; also for the extraction of oil, the preservation of anatomical preparations, the carburation of illuminating gas, and for the preparation of lacquers and varnishes. *Ligroïn* is a similar distillate used for feeding the so-called 'Ligroïn or Wonder-lamps.'

Artificial Turpentine-oil, Petroleum-spirit, Polishing Oil: distillate between 120° – 170° ; obtained also with superheated steam; sp. gr. 0.740–0.745; does not dissolve resins; used for diluting linseed-oil varnish and for cleaning printers' type.

Illuminating Oil, Petroleum, Kerosene, Paraffin Oil, Refined Petroleum, has a large and increasing consumption for lamps, also for warming greenhouses, &c.; sp. gr. 0.78 to 0.81; flashing point (in the open vessel) 90° – 110° F.; igniting point 110° – 130° F.; includes all the intermediate distillates from crude petroleum, ranging from sp. gr. 0.76 to 0.83. The finest-quality of illuminating oil is produced from distillates ranging only from 0.775 to 0.790; this, when treated by aeration, is the water-white high-test oil used largely by the higher classes in America. It has a very high flashing point (120° – 140° F. in the open vessel), as it contains none of the lighter parts of the crude oil.

Lubricating Oil.—Sp. gr. 0.850 to 0.915; of a pale amber colour; coming largely into use as an efficient lubricant in combination with rape, olive, or lard oil. The best qualities have a sp. gr. of about 0.895, the heavier oils from 0.900 to 0.915 containing solid paraffin.

The residues of the distillation are utilised for gas-making.

The present production of petroleum in the United States only, exceeds 50,000 barrels or 2,500,000 American gallons daily. The quantity exported thence during the year 1879 exceeded 400,000,000 gallons. See Martius (*Dingl. pol. J.* cxxxv. 504; *Jahresh. f. Chem.* 1877, 1218).

Russian Petroleum from the Caucasus (K. Linenko, *Dingl. pol. J.* cxxxvii. 78, 161). The district surrounding Baku, a city on the borders of the Caspian Sea, is the seat of the petroleum industry of the Caucasus. The regular extraction of this oil commenced in 1872, and 65,000 tons of kerosene from 200,000 tons of crude petroleum is the annual production at the present time. The crude oil of this district comes from springs not more than from 90 to 120 meters deep, and has a sp. gr. of 0.860 to 0.875; it yields only 33 to 35 per cent. of oil for lighting purposes; the remaining naphtha-residue has lately come into request for raising steam in the steam-ships of the Lower Volga and the Caspian Sea.

The refined oil of Baku is distinguished from the American by its greater density at 14° , the former being 0.820, the latter 0.800.

The following table (p. 1510) shows the results of comparative experiments on the Russian and American oils. Three kinds of Russian oil were experimented on. The 3rd kind is the heavy kerosene, manufactured for Persian consumption; the 2nd is an ordinary commercial variety; while No. 1 is prepared only in small quantities. No. 2 is a clear and slightly fluorescent liquid with a not disagreeable odour. The American varieties tested were of two kinds—1st, the ordinary variety, of a yellow colour; and 2nd, the high-test, which also goes by the name of *Australöl* and *Oleophin*. The numbers show that the hydrocarbons in the Russian oil are more volatile than those in the American. None of them were obtained quite pure.

The mineral oils of Buxière-la-Grue and of Cordesse, in Alsace, have been examined by J. Joffe (*Bull. Soc. Chim.* [2], xix. 547). They differ from American petroleum in being partly absorbed by fuming sulphuric acid, and converted by nitric acid into nitro-products. About 50 per cent. of these oils consists of paraffin-oils, and is not attacked by these reagents; the hydrocarbons, C^8H^{18} and $C^{17}H^{36}$, were isolated by fractional distillation. The portions of these mineral oils which are absorbed by sulphuric acid consist of olefines, C^8H^{16} , or of hydrocarbons containing a still smaller proportion of hydrogen. They do not contain either benzene or naphthalene.

Egyptian petroleum differs from the American by its much greater density

Comparison of Russian and American Petroleum.

	Baku No. 3	No. 2	No. 1	Ordinary Kerosin Baku	Australal	Ordinary American Oil
Specific gravity	At 16.5° 0.842	At 14° 0.822	At 19° 0.802	At 14° 0.822	At 14° 0.788	At 16° 0.795
Percentage of distillate at 200°	At 2.5° 0.854	At 2.5° 0.831	At 2.5° 0.815	At 2.5° 0.832	At 2.5° 0.794	At 2.5° 0.804
" " " 280°	— 76.4	33.4 80.4	65.6 92.6	31.2 80.4	37.8 85.0	25.0 52.8
Specific gravity of distillate at 200°	—	At 20° 0.787	At 20° 0.790	At 18° 0.789	At 20° 0.766	At 19° 0.753
" " " 280°	At 19° 0.835	At 20° 0.831	At 19° 0.822	At 18° 0.832	At 20° 0.785	At 19° 0.786
Percentage of distillate at 100°	—	(Boiling point)	—	(Boiling point)	—	(Boiling point)
From 100° to 120°	—	0.8	0.1 (Boiling point)	0.8	—	0.8
" 120° to 140°	—	7.8	0.6 24.9	8.8	0.2 (Boiling point)	6.6
" 140° to 160°	—	21.2	48.0	20.8	3.0	16.0
" 160° to 180°	(Boiling point)	33.4	65.5	31.2	27.8	25.0
" 180° to 200°	13.6	45.0	76.6	44.0	48.0	30.2
" 200° to 220°	38.8	57.8	84.2	56.2	63.8	34.8
" 220° to 240°	(Yellow)	70.0	88.8	69.6	75.2	44.2
" 240° to 260°	62.0	(Colourless)	(Colourless)	(Colourless)	85.0	(Yellowish)
" 260° to 280°	(Yellow)	80.4	92.6	80.4	85.0	52.8
" 280° to 300°	76.4	(Yellowish)	(Colourless)	(Yellowish)	11.8	(Yellow)
" 300° to 320°	(Yellow)	15.6	2.6	14.8	—	41.8
Residue	20.9	(Golden yellow)	(Golden yellow)	(Golden yellow)	3.2	(Brown)
Loss	(Brown)	3.0	4.8	4.8	52.2°	5.4
Evaporating point	3.3	28°	25.5°	Not determined	—	28.5°
	Not determined	—	—	—	—	—

and by not containing the lighter oils or the ordinary burning oil of sp. gr. 0·8. It yields however an excellent lubricating oil, and in its crude state is well adapted for heating steam boilers, its use involving but little risk of fire (F. Weil, *Monit. scient.* cccxvi. 432).

Sulphur in Petroleum. According to H. Vohl (*Dingl. pol. J.* cccvi. 47) all kinds of petroleum contain sulphur, and may be purified therefrom by treatment with acids and alkalis. The impurity is most easily detected by heating the petroleum with metallic sodium. If sulphur is present, the bright metal soon becomes covered with a yellow crust of sodium sulphide, which may be dissolved off by water and tested. The quantity of the sulphur may be estimated by distilling the petroleum over red-hot lime, and subsequently weighing the sulphur as barium sulphate. Vohl found in different kinds of petroleum from 0·300 to 3·114 per cent. of sulphuric acid.

On the use of the heavier petroleum oils, *Vulcan oil*, *Opal oil*, &c., as lubricators, see OILS (p. 1429); also J. J. Coleman (*Dingl. pol. J.* ccx. 195; *Jahresb. f. Chem.* 1873, 1094).

Use of Petroleum for Illumination.—Experiments on the comparative cost of a given amount of light from petroleum oil, colza-oil, and coal-gas have lately been made by Messrs. B. and T. H. Redwood (*Chemist and Druggist*, Dec. 15, 1879, p. 540). The following table exhibits the mean results for 1000 ‘candle-hours,’ that is to say, for the amount of light which would be obtained by burning a standard sperm candle for 1000 hours.

Cost of 1000 ‘Candle-hours.’

From petroleum-oil at per gallon					From colza-oil at per gallon				From coal-gas at per 1000 cubic feet			
9d.	1s.	1s. 3d.	1s. 6d.		3s.	3s. 6d.	4s.		3s.	3s. 6d.	4s.	
7½d.	9¾d.	11¼d.	1s. 3d.		2s. 4d.	2s. 8d.	3s. 0¾d.		1s. 3d.	1s. 5½d.	1s. 8d.	

These numbers show that, taking petroleum-oil at 1s. per gallon, and colza-oil at 3s. 6d. per gallon, the cost of a given amount of light is more than three times greater for the latter than for the former; and that, taking petroleum at 1s. per gallon and coal-gas at 3s. 6d. per 1000 cubic feet, a given amount of light from the former costs only about half what it does when obtained from the latter, while there is the additional advantage that properly purified petroleum-oil in burning does not produce sulphur-compounds.

Flashing Point of Petroleum.—This term is used to denote the temperature at which any sample of petroleum or its products begins to give off inflammable vapours. The more volatile kinds give off such vapours even at ordinary temperatures, and these vapours when mixed with air form explosive mixtures: hence the use of such oils for burning in lamps is attended with great danger. To prevent accidents from this cause, it was enacted by the American Petroleum Act, and by the British Petroleum Act of 1871, that no petroleum-oil should be used for burning in lamps which gives off inflammable vapours at any temperature below 100° F. (or 38° C.) when tested in an open cup described in the Schedule of the Act. The great increase in the consumption of the article between the years 1871 and 1877, however, necessitated the adoption of a system of testing less liable to variation in the hands of different operators. This question having been referred to Professor Abel, he proposed the use of a closed vessel to be heated by hot water, with a standard flashing-point of 73° F., which was found to be the equivalent of 100° on the open cup system.* This proposal, being favourably reported on by the Petroleum Trade Association, was eventually adopted as the basis of the new Petroleum Act of 1879.

The testing apparatus above mentioned consists of a small closed oil-cup fitting into a water-bath. On the top of the cup is a brass slide, and a minute oil-lamp with a jet. A thermometer is also fixed with its bulb in the oil cup. The operator watches the thermometer, and at intervals draws out the brass slide, thus causing a jet of flame to dip into the oil-cup. The ‘flashing point,’ or temperature at which the petroleum begins to give off an inflammable vapour, is thereby ascertained. This apparatus is accurately described and figured in the schedules of the new Act. (See also *Chemist and Druggist*, Dec. 15, 1879, p. 541; *Chem. News*, xl. 305).

* It will be observed that the standard is not lowered by this alteration, but simply adjusted to the new system. More than 1000 samples were tried on the two systems, the variations ranging from 26° to 29° F.; hence 27° was adopted as the mean variation, making the standard 73° instead of 100°.

Gas from Petroleum.—The value of petroleum and coal-tar for the production of gas has been studied by A. Wagner (*Dingl. ccxvi.* 250). Experimenting with a petroleum which began to boil at 150°, he found that when the vapours given off below 288° were passed through a red-hot porcelain tube filled with lumps of pumice-stone, the petroleum was resolved into $\frac{1}{3}$ gas, $\frac{1}{3}$ condensed products, and $\frac{1}{3}$ residue left in the retort. The gas consisted of 5.0 vol. p. c. acetylene, 35.96 heavy, and 59 light hydrocarbons. Wagner is of opinion that the first product of the decomposition of the petroleum at high temperatures is ethylene, which is partly decomposed according to the equation $C^2H^4 = CH^4 + C$, and that the methane thus produced is further decomposed, yielding acetylene and hydrogen: $2CH^4 = C^2H^2 + 3H^2$. Petroleum-ether yields a larger quantity of gas than crude petroleum. 1 gram of petroleum yielded 0.876 lit. gas; 1 gram of petroleum-ether gave 0.916 lit. gas.

Wagner rejects as worthless all projects for making gas by distilling petroleum mixed with wood, peat, charcoal, &c., because the dry distillation of these solid substances always produces water, which in evaporating carries the petroleum along with it, before the petroleum can be converted into gas. The only rational way of converting petroleum into gas is to heat it by itself, and in this operation a high temperature of the retorts is an indispensable condition.

Petroleum gas when burnt alone requires burners with small apertures; it is very well adapted for heightening the illuminating power of gas of inferior quality. The production of an illuminating power of 136 kilos. of stearin requires a quantity of gas obtained from 1 cwt. of petroleum or from 2.6 cwt. of Boghead coal.

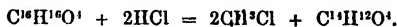
The composition of the gas emitted from certain petroleum springs in West Pennsylvania has been determined by S. P. Sadtler (*Amer. Chem.* vii. 97):

	Burns Gas-well	Leecburbgh Gas-well	Harrey well	Cherry-tree well
Carbon dioxide	0.34	0.35	0.66	2.28
Carbon monoxide	traces	0.26	traces	—
Olefines	—	0.56	—	—
Methane	75.44	89.65	80.11	60.27
Hydrogen	6.10	4.79	13.50	22.50
Ethane	18.12	4.39	5.72	6.80
Propane	traces	traces	traces	—
Oxygen	—	—	—	0.83
Nitrogen	—	—	—	7.32

See also GASES (p. 858).

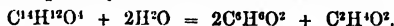
PETZITE. See TELLURIUM MINERALS.

PEUCEDANIN, $C^{16}H^{16}O^4$, and **OROSELONE**, $C^{14}H^{12}O^4$ (iv. 216, 386). The composition and mutual relations of these bodies have been further examined by Hlasiwetz a. Weidel (*Liebigs Annalen*, clxxiv. 67). By decomposing an alcoholic solution of peucedanin with hot aqueous hydrochloric acid, and by passing dry hydrochloric acid gas over peucedanin, they obtained oroselone, the reaction in the latter case being attended with the evolution of a gas (probably methyl chloride) which burned with a green-edged flame:



Angelic acid, which was stated by Wagner to be formed in the decomposition of oroselone with potash, was not obtained by Hlasiwetz a. Weidel, either in the reaction just mentioned, or by decomposing oroselone with alcoholic potash.

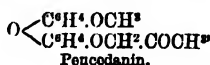
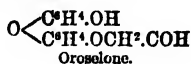
Oroselone fused with potash yields resorcinol and acetic acid:



Peucedanin fused with potash yields only a small quantity of resorcinol.

Oroselone is readily attacked by *acetyl chloride* and *valeryl chloride*, yielding monacetyl-oroselone, $C^{14}H^{11}(C^2H^3O)O^4$, and monovaleryl-oroselone, $C^{14}H^{11}(C^4H^7O)O^4$, respectively. The former crystallises in slender colourless needles, melting at 123°; the latter forms large rhombic prisms melting at 95°–97°, and is not identical with athamantin (i. 430). Monovaleryl-oroselone is decomposed by gaseous hydrogen chloride into valeryl chloride and oroselone.

The relation between peucedanin and oroselone may perhaps be represented by the following formulæ:



Oroselone may be regarded as an aldehydic compound, and peucedanin as a corresponding ketone analogous thereto.

PHACOLITE. This variety of chabasite, originally found at Leipa in Bohemia (i. 844), occurs also in a basaltic conglomerate in the neighbourhood of Giessen. Six analyses by Burkhardt a. Hammerschlag gave as a mean result:

SiO ^a	Al ^a O ^a	Fe ^a O ^a	CaO	K ^a O	Na ^a O	H ^a O (?)	H ^a O (?)
46·82	19·29	0·14	10·29	0·14	0·70	14·98	7·38

(^a) Given off up to 300°.

(?) Above 300°.

(A. Streng, *Jahrb. f. Min.* 1877, 725).

Seebachite from Richmond in Victoria (vii. 1077) is regarded by G. vom Rath (*ibid.* 1876, 63) as identical with phacolite; he finds that it belongs to the rhombohedral system, has a density of 2·135, and gives by analysis:

SiO ^a	Al ^a O ^a	CaO	K ^a O	Na ^a O	H ^a O
46·08	21·09	5·76	1·77	4·52	21·08 = 100·29

leading to the formula,



which requires 46·71 SiO², 20·00 Al²O³, 5·46 CaO, 2·29 K²O, 4·52 Na²O, and 21·02 H²O. An analysis of seebachite by Lepsius (*Jahresb. f. Chem.* 1874, 1264) gave 44·77 SiO², 22·10 Al²O³, 7·51 CaO, 3·18 Na²O, and 22·07 H²O = 99·63.

PHÆACTINITE. A radiate transformation product of hornblende, forming one of the constituents of the isenite of Nassau (see ISENITE, p. 1126).

PHARMACOLITE. Native calcium arsenate (iv. 387). According to measurements by A. Schrauf (*Jahrb. f. Min.* 1873, 616) the crystals are monoclinic, having the axial ratio $a : b : c = 0·613727 : 1 : 0·362226$, and the angle $a c = 96^\circ 46\frac{1}{2}'$.

Picropharmacolite, hitherto regarded as a pharmacolite, appears from analyses by A. Frenzel (*ibid.* 1873, 786) to be a distinct mineral species. The microcrystalline, probably monoclinic, mineral occurs in white groups rarely coloured blue by copper, on copper pyrites, gneiss, and even on the timbering of the 'hohe Birke' and 'Kröner' mines at Freiberg.

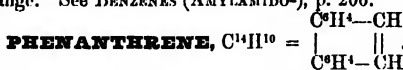
A. Analysis. B. Values calculated from the formula $5\text{CaO}·2\text{As}^2\text{O}^3 + 12\text{H}^2\text{O}$:

As ^a O ^a	CaO	MgO	H ^a O
A. 46·93 (¹)	25·77	3·73	24·01 (²) = 100·44
B. 48·11	29·29	—	22·60 = 100

(¹) A check analysis gave 48·14 per cent.

(²) 13 per cent. given off at 100°.

PHENAMYLAMINE, or *Amido-amyl-benzene*, $\text{C}^6\text{H}^4(\text{C}^6\text{H}^{11})\text{NH}^2$. A base isomeric with amylaniline, and produced therefrom by intramolecular atomic interchange. See BENZENES (AMYLAMIDO-), p. 206.



PHENANTHRENE, $\text{C}^{14}\text{H}^{10}$ = $\begin{array}{c} \text{C}^6\text{H}^4\text{—CH} \\ | \quad | \\ \text{C}^6\text{H}^4\text{—CH} \end{array}$. *Diphenylene-ethylene*.—This hydro-

carbon, isomeric with anthracene, has already been described in connection with the latter (vii. 84; viii. 95), but many important observations relating to it have lately been published.

Phenanthrene is one of the constituents of the substance called 'idryl,' obtained by the dry distillation of an Idrian quicksilver ore (p. 1084).

Ostermayer (*Ber.* vii. 1089) prepares phenanthrene by subjecting crude anthracene to slow fractional distillation, collecting the portion which passes over between 320° and 350°, boiling it with a large quantity of alcohol, and leaving the solution to crystallise. The first crystallisation must be rejected, as it consists chiefly of anthracene; but the product obtained from the mother-liquor consists, after two recrystallisations from alcohol, of nearly pure phenanthrene melting at 98°–100°. Phenanthrene obtained by treating the dibromide (vii. 85) with alcoholic potash, melts at 96°, and the same melting point is exhibited by phenanthrene obtained by heating phenanthraquinone with zinc-dust.

On the purification of phenanthrene, see also Hayduck (*Liebig's Annalen*, clxvii. 177; *Ber.* vi. 532; *Jahresb. f. Chem.* 1873, 394).

Action of Chlorine.—By exhaustive chlorination with chlorine and iodine (p. 1066), phenanthrene is decomposed like anthracene, yielding perchlorobenzene and perchloromethane, the formation of these bodies being perhaps preceded by that of perchlorophenanthrene (Rüoff, *Ber.* 1048).

Phenanthrene Dibromide and Bromophenanthrene (Hayduck, *Liebig's Annalen*, clxvii. 180). The *dibromide*, $\text{C}^{14}\text{H}^{10}\text{Br}^2$, which Fittig a. Ostermayer obtained

by dropping bromine into an ethereal solution of phenanthrene (vii. 85), may also be prepared by dissolving the calculated quantities of phenanthrene and bromine in carbon sulphide, and slowly mixing the solutions after cooling them with ice, and separates after a few hours in well-defined flat four-sided prisms which, after washing with a little cold carbon sulphide, and pressing between paper, are nearly white. It slowly decomposes when kept, turning brown and giving off hydrogen bromide; melts at 98° with brisk effervescence and evolution of hydrogen bromide, and is converted into monobromophenanthrene. Solution of silver nitrate added to the cold alcoholic solution forms a precipitate of silver bromide. Heating with alcohol produces immediate decomposition. According to Anschütz (*Ber.* xi. 1217), the dibromide treated with nitric acid in acetic acid solution, appears to yield a nitro-product. Dissolved in alcohol and treated with potassium cyanide, it yields phenanthrene.

Monobromophenanthrene, $C^{14}H^9Br$, is formed, as above described, by the action of heat on the dibromide, also by heating that compound with water. To prepare it, the dibromide is heated on a water-bath as long as hydrogen bromide continues to escape, and the residue is dissolved in hot strong alcohol, from which it separates as an oil which quickly solidifies to a crystalline mass. From weaker solutions it crystallises in thin white prisms, which melt at 63° , and dissolve readily in glacial acetic acid and carbon sulphide. The alcoholic solution exhibits a slight fluorescence. Bromophenanthrene may be sublimed without decomposition; it does not give off bromine when heated for several hours with alcoholic potash, but when heated with sodium amalgam in alcoholic solution it yields sodium bromide and phenanthrene.

The carbon sulphide from which phenanthrene dibromide, prepared as above, has crystallised out, still retains bromine-compounds which remain as a soft brown mass on distilling off the solvent. Cold ether decomposes this brown substance into an easily soluble oily compound and a yellowish powder which remains undissolved. The oily compound, which retained its dark colour even after repeated attempts at purification, gave by analysis 31.5 per cent. bromine, answering to the formula of monobromophenanthrene. It was not altered by boiling with alcoholic potash, or apparently by sodium-amalgam in alcoholic solution. Bromine decomposes it with evolution of hydrogen bromide, but the product is an uncrystallisable resin.

Dibromophenanthrene, $C^{14}H^8Br^2$.—This is the composition of the above-mentioned yellow powder insoluble in ether; it is formed in small quantity only. It dissolves sparingly in hot alcohol, and separates from solution in glacial acetic acid in the form of a yellowish-white indistinctly crystalline powder melting at 202° . Another dibromophenanthrene is formed on adding bromine to a solution of the monobromo-derivative in carbon sulphide. The reaction goes on to the end, with evolution of hydrogen bromide, even at ordinary temperatures; and on distilling off the carbon sulphide after a few hours, and dissolving the residue in warm alcohol, dibromophenanthrene separates on cooling in nodular groups of white needles (still retaining a little of the monobromo-derivative), which melt at about 110° and gradually soften even below this temperature (Hayduck).

Two other dibromophenanthrenes are described by Zetter (*Ber.* xi. 164). One of these, formed by the action of bromine on phenanthrene in ethereal solution, crystallises from alcohol in long needles, melts at 148° , and sublimes in yellow needles. Most solvents dissolve it readily, and deposit it in crystals when evaporated. Another formed together with the last, crystallises in tables which melt at 158° , and do not sublime even when strongly heated. It dissolves easily in the ordinary solvents, and crystallises from the solution on evaporation. Neither of these dibromo-compounds is attacked by boiling alcoholic potash.

Tribromophenanthrene, $C^{14}H^7Br^3$, is formed when a solution of the dibromo-compound in carbon sulphide is heated with bromine for several hours in a reflux apparatus. The product which remains on evaporating off the carbon sulphide crystallises from hot glacial acetic acid in very slender white silky needles, melting at 126° . On heating it with bromine to 140° in sealed tubes, further bromination takes place, yielding products which are nearly insoluble in cold alcohol and glacial acetic acid, slightly soluble in benzene, more readily in hot xylene, from which they separate as a white long-fibred crystalline mass, which does not melt at 290° (Hayduck). Zetter obtained the same dibromophenanthrene by heating phenanthrene to 130° – 140° with the calculated quantity of bromine.

Tetrabromophenanthrene, $C^{14}H^6Br^4$, is produced when phenanthrene is heated to 200° – 210° with the requisite quantity of bromine. It forms small granular crystals, which melt at 183° – 185° , and dissolve in benzene and toluene, but scarcely in alcohol or ether (Zetter).

Hexbromophenanthrene, $C^{14}H^4Br^6$, is formed on heating phenanthrene to 280° with the calculated quantity of bromine and 1 mol. of iodine. It sublimes in snow-white

needles, which melt at 245° , and dissolve in glacial acetic acid, benzene, and toluene (Zetter).

Heptabromophenanthrene, $C^{14}H^9Br^7$, is produced by heating phenanthrene, with excess of bromine containing iodine, to 300° , or a higher temperature, in sealed tubes. It sublimes in small yellowish needles, which melt above 270° (Zetter).

Chlorophenanthrenes (Zetter, *loc. cit.*) A solution of phenanthrene in glacial acetic acid absorbs chlorine readily in the cold, and gives off hydrogen chloride. The product of the reaction consists mainly of dichlorophenanthrene tetrachloride, but contains also dichloro- and monochloro-phenanthrene.

Dichlorophenanthrene tetrachloride, $C^{14}H^8Cl^2Cl^4$, crystallises in small colourless needles, which dissolve very easily in alcohol, ether, benzene, and toluene, melt at 145° , and give off hydrogen chloride at a slightly higher temperature. When heated with alcoholic potash, it loses first one and then a second atom of chlorine, yielding tetrachlorophenanthrene.

Monochlorophenanthrene, $C^{14}H^9Cl$, is an oily liquid, easily soluble in the liquids named above, but not in water. It carbonises when slightly heated.

Dichlorophenanthrene, $C^{14}H^8Cl^2$, is an amorphous white substance, easily soluble in glacial acetic acid, ethyl acetate, alcohol, ether, benzene, and toluene. It melts to a transparent oily liquid at a low temperature.

Tetrachlorophenanthrene, $C^{14}H^6Cl^4$, is formed by the action of antimony pentachloride on phenanthrene in the cold, or by the action of iodine chloride at 100° – 110° . It crystallises in small yellowish needles, which dissolve easily in ether, benzene, and toluene, but very slightly in alcohol. The crystals melt at 171° – 172° , and sublime in thin yellowish needles. Neither this nor any of the higher chlorinated products is affected by boiling with alcoholic potash.

Hexachlorophenanthrene, $C^{14}H^4Cl^6$, is formed by the action of antimony pentachloride on phenanthrene in closed tubes at 120° – 140° , or in the oil-bath at 180° – 200° . It sublimes in white feathery crystals, which melt at 249° – 250° , and dissolves very sparingly in alcohol, ether, and acetic acid.

Octachlorophenanthrene, $C^{14}H^2Cl^8$, is produced on heating phenanthrene with excess of antimony pentachloride to 180° – 200° . It crystallises in indistinct granular forms, and sublimes in yellow needles, which melt at 270° – 280° . It is nearly insoluble in alcohol and ether, but dissolves easily in benzene and toluene.

Nitro- and Amidophenanthrenes (G. A. Schmidt, *Ber.* xii. 1153). Three mononitrophenanthrenes are obtained when nitric acid (sp. gr. 1.35) is allowed to act slowly on phenanthrene mixed with sand, and may be separated, though with great difficulty, by fractional crystallisation from alcohol, ether, toluene, and glacial acetic acid.

α -Mononitrophenanthrene, $C^{14}H^9(NO^2)$, is obtained in largest quantity, and is identical with the mononitrophenanthrene described by Graebe (vii. 85). It crystallises from alcohol or glacial acetic acid in straw-yellow needles melting at 74° (at 70° – 80° according to Graebe). The presence of small traces of impurities causes it to remain liquid even at very low temperatures. By reducing it with tin and hydrochloric acid, or with alcoholic ammonium sulphide, *α -amidophenanthrene hydrochloride*, $C^{14}H^9(NH^2).HCl$, is obtained as a white crystalline precipitate, which is sparingly soluble in water, and is rapidly decomposed on exposure to the air. The *sulphate*, $(C^{14}H^9.NH^2)H^2SO^4$, is much more stable, and consists of a white powder sparingly soluble in alcohol and in water.

α -Amidophenanthrene is insoluble in water, and crystallises from dilute alcohol in small yellow plates.

α -Mononitrophenanthraquinone is formed by the oxidation of the nitro-compound with chromic and acetic acids. It crystallises in brilliant orange-yellow plates (m. p. 215° – 220°), which are insoluble in water and sparingly soluble in alcohol, ether, and benzene, but more easily in glacial acetic acid.

β -Mononitrophenanthrene, $C^{14}H^9(NO^2)$, differs but little in appearance and solubility from the α -compound, although it is somewhat less soluble in ether than the latter. It is obtained in smaller quantity than either of the other isomerides, and melts at 127° . Unlike the α -compound, it is only acted on with difficulty by alcoholic ammonium sulphide, and is best reduced by tin and hydrochloric acid in alcoholic solution. *β -Amidophenanthrene hydrochloride* forms a moderately stable crystalline mass, which is sparingly soluble in water. *β -Amidophenanthrene* crystallises from alcohol in small brilliant plates. *β -Mononitrophenanthrene* is more difficult of oxidation than the α -compound, and gives a product which crystallises from glacial acetic acid in brilliant orange-yellow needles (m. p. 260° – 266°).

γ-Mononitrophenanthrene, $C^{14}H^9(NO^2)$, crystallises in small brilliant plates (m. p. 170°), which are of a darker yellow colour, and are more sparingly soluble in ether and alcohol than the α - or β -compound.

γ-Amidophenanthrene hydrochloride, $C^{14}H^9(NH^2).HCl$, obtained by reduction of the nitro-compound with alcoholic ammonium sulphide, forms yellowish brilliant crystals. The free base resembles the α - and β -compounds.

On oxidation with chromic and glacial acetic acids, γ -nitrophenanthrene gives a compound which crystallises in dark orange-yellow needles (m. p. 263°), which are only very sparingly soluble in alcohol, but easily in glacial acetic acid.

Dinitrophenanthrene, $C^{14}H^8(NO^2)_2$, is obtained by prolonged action of nitric acid on phenanthrene at 100° ,—also, together with the mononitro-derivative, when the temperature is not kept low enough in the preparation of the latter. It crystallises from glacial acetic acid and melts at 150° – 160° (Graebe).

Nitrobromophenanthrenes.—When monobromophenanthrene dissolved in glacial acetic acid is warmed with nitric acid, a mixture of at least two nitro-compounds is precipitated on the addition of water, in the form of yellow microscopic needles. From this mixture, carbon sulphide or ether extracts one of the bodies, and leaves the other as a reddish-yellow substance, which has not been further examined. The soluble portion after recrystallisation yields fine prisms or compact crystals of *mononitrobromophenanthrene*, $C^{14}H^8(NO^2)Br$, melting at 195° and subliming in long needles (Anschütz, *Ber.* xi. 1207).

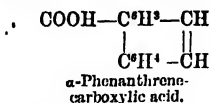
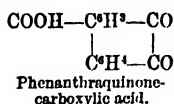
Hydroxyphenanthrene, or Phenanthrol, $C^{14}H^{10}O = C^{14}H^9(OH)$. This compound is obtained by treating phenanthrene with the calculated quantity of fuming sulphuric acid, converting the resulting monosulphonic acid into an ammonium salt, and fusing the latter with potash. The product crystallises from a mixture of benzene and petroleum-spirit in thin laminae, which exhibit a bluish fluorescence, and melt at 112° .

Phenanthrol dissolves easily in alcohol and ether, less easily in benzene, and slightly in water. On exposure to air it acquires a red to brown colour. Alkalis dissolve it easily, forming crystalline compounds, which are readily soluble in water.

With acetic and benzoic anhydrides phenanthrol forms ethers which crystallise well. The *acetyl-compound*, $C^{14}H^9O(C^2H^3O)$, obtained by heating phenanthrol to 150° with acetic anhydride, crystallises from alcohol in shining laminae, which melt at 117° – 118° (G. Rehs, *Ber.* x. 1252).

Phenanthrene-carboxylic Acid, $C^{14}H^9.COOH$. Of this acid there are two modifications distinguished as α and β . The first, discovered by Japp a. Schultz (*Ber.* x. 1661), is obtained by converting crystallised calcium phenanthrenesulphonate into the corresponding sodium salt, distilling the latter with potassium ferrocyanide, saponifying the resulting nitril with alcoholic potash, and acidifying the solution with hydrochloric acid, which throws down the phenanthrene-carboxylic acid in bulky white flocks. It is nearly insoluble in water, but dissolves easily in alcohol, ether, and glacial acetic acid, melts at 260° , and sublimes with partial decomposition. Its alkali-salts are easily soluble in water. The barium salt, $(C^{14}H^9COO)^2Ba + H^2O$, dissolves easily in hot water, and crystallises therefrom in tufts of needles.

By distillation with soda-lime, the acid is converted into phenanthrene, and by oxidation with chromic acid in acetic acid solution it is converted into phenanthraquinone-carboxylic acid; this determines its formula as under:



β -Phenanthrene-carboxylic acid, discovered by Japp (*Chem. Soc. J.* 1880, xxxvii. 83), is obtained from the dark syrupy mother-liquor which remains after the crystallisable calcium phenanthrenesulphonate above-mentioned has separated out. This mother-liquor contains an isomeric calcium phenanthrenesulphonate; and on converting it into sodium salt, distilling this salt in the dry state with $1\frac{1}{2}$ times its weight of potassium ferrocyanide, and boiling the resulting nitril with alcoholic potash for more than 100 hours, with inverted condenser, then distilling off the alcohol, digesting the contents of the flask with water, diluting, filtering, and acidifying with hydrochloric acid, β -phenanthrene-carboxylic acid separates out as a dirty-white flocculent precipitate (above 80 grams from 2 kilos. of commercial phenanthrene). It is most readily purified by converting it into the sodium salt, recrystallising this salt till it is quite colourless, and acidulating its solution with hydrochloric acid, which throws down the β -acid as a white flocculent precipitate.

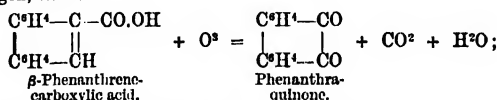
β -Phenanthrene-carboxylic acid is soluble in alcohol, ether, and glacial acetic acid

almost insoluble in water. From a hot saturated solution in acetic acid, it crystallises in stellate groups of colourless needles.

The following table exhibits a comparison of the physical characters of the two phenanthrene-carboxylic acids and of their sodium and barium salts. Most of the crystallographical characteristics can be perceived only with the aid of a microscope :

	α -Acid	β -Acid
Acid . .	Crystallises from hot glacial acetic acid in colourless, curved blades, with parallel edges, and a rectangular termination. This curvature is very characteristic. Sublimes in fern-shaped leaves. M. p. 266°.	Crystallises from hot glacial acetic acid in stellate groups of colourless, straight, pointed needles. Sublimes in fern-shaped leaves. M. p. 250°-252°.
Sodium salt.	$C^{14}H^9.CO^2Na + 4H^2O$. Tufts of colourless, pointed blades. 100 parts of water at 20° dissolves 6·8 parts of the anhydrous salt. Almost indefinitely soluble in boiling water.	$C^{14}H^9.CO^2Na + 5H^2O$. Colourless, rhomboidal laminae, with a slightly satiny lustre. 100 parts of water at 20° dissolve 6·2 parts of the anhydrous salt. Almost indefinitely soluble in boiling water.
Barium salt.	$(C^{14}H^9CO^2)^2Ba + 7H^2O$. Colourless, long needles of extraordinary fineness and flexibility, radiating from one point to form large balls or tufts. Under the microscope a tangled mass of these flexible needles has the appearance of vegetable fibre. 100 parts of water dissolve— At 20° . . 0·066 } part of anhy- ,, 100° . . 5·60 } drous salt.	$(C^{14}H^9.CO^2)^2Ba + 6H^2O$. Colourless, long, brittle, rectangular laminae, united in a ramiform crystallisation. 100 parts of water dissolve— at 20° . . 27 } parts of anhy- ,, 100° . 3·70 } drous salt.

The β -acid is converted by oxidation with chromic acid into phenanthraquinone, with elimination of the carboxyl-group: consequently it must contain this group attached to one of the carbon-atoms which in the quinone are united to the quinonoid oxygen, thus :



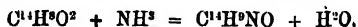
and the sulphonic acid from which it is derived must be represented by a similar formula with $SO^2.OH$ in place of $CO.OH$.

Phenanthraquinone, $C^{14}H^8O^2 = \begin{array}{c} C^6H^4-CO \\ | \quad | \\ C^8H^4-CO \end{array}$. The preparation, properties,

and principal reactions of this compound have already been described (vii. 92-95). When distilled with dry *soda-lime*, it is almost completely converted into diphenyl, but when the *soda-lime* contains a considerable amount of moisture, fluorene, fluorene alcohol, diphenylene ketone, and a red body are formed. The latter result is explained by the fact that the water and soda in the *soda-lime* convert the phenanthraquinone into diphenylene ketone and diphenylene-glycollic acid, which latter decomposes, yielding fluorene alcohol, $(C^8H^9)^2.CHOH$ (p. 673). Heated with quicklime, phenanthraquinone forms fluorene and diphenylene ketone. In the same way when diphenic acid, $C^{14}H^{10}O^4$, is distilled with quicklime, it yields diphenylene ketone, a red body, and traces of diphenyl, but when heated with a mixture of slaked and quicklime, it gives diphenylene ketone, diphenyl, and a red body, whilst with slaked lime, *soda-lime*, or zinc-dust, it yields diphenyl and only a trace of the red body (Anschütz a. Schultz, *Ber.* ix. 1400).

Alcoholic potash converts phenanthraquinone into diphenic acid, $C^{14}H^{10}O^4$; with *alcoholic ammonia* it yields phenanthraquinonimide, $\begin{array}{c} C^6H^4-CN^H \\ | \quad | \\ C^8H^4-CO \end{array}$, which

crystallises in brownish needles melting at 167°. Its formation is represented by the equation :



By strong hydrochloric or sulphuric acid the imide is reconverted into phenanthraquinone. When phenanthraquinone is heated with alcoholic ammonia for several days in sealed tubes, a mixture of several substances is obtained, one of which has the composition $C^{14}H^{10}N^2$, and forms dark-green or brown needle-shaped crystals, slightly soluble in amyl alcohol (Anschütz a. Schultz, *Liebig's Annalen*, cxvi. 49-53). E. Schmidt (*Ber.* vii. 1365), by treating phenanthraquinone with aqueous ammonia, obtained two compounds represented by the formulæ $C^{14}H^{11}N^2O^2$ and $C^{12}H^{10}N^2$.

Oxidation by Permanganate.—Phenanthraquinone, treated with very weak soda-ley and potassium permanganate at 100°, yields diphenylene ketone. When boiled with weak soda-ley alone it yields diphenylene-glycollic acid, and when heated with dilute solution of permanganate alone it yields diphenic acid. Diphenylene ketone and diphenic acid, when further oxidised with alkaline permanganate, yield phthalic acid, but apparently no isophthalic or terephthalic acid. The same product was obtained also by the oxidation of sodium phenanthreno-sulphonate with potassium permanganate (Anschütz a. Japp, *Ber.* xi. 211).

Action of Zinc-ethyl.—When finely powdered phenanthraquinone is gradually added to zinc-ethyl diluted with ether to such an extent that it is no longer spontaneously inflammable, a reaction takes place accompanied by evolution of gas and precipitation of a whitish powder. The addition of the quinone must be continued so as nearly to exhaust the zinc-ethyl, but leave it in slight excess. On decomposing the product with excess of alcohol, boiling, and filtering hot, a substance is obtained having the composition $C^{16}H^{14}O^2.C^2H^6O$, in transparent nearly colourless rectangular plates, often nearly an inch long, sometimes grouped in rosettes. It begins to soften at 73° and melts at 77°; dissolves readily in all the ordinary solvents except water, which takes up only traces of it. Exposed to the air for some days in the finely divided state, it gradually changes to a deep orange-coloured gummy mass; in a vacuum, however, it remains unaltered.

The compound $C^{16}H^{14}O^2$ has not been obtained in the pure state, inasmuch as the last traces of alcohol cannot be expelled without decomposing it; but its *acetyl-derivative*, $C^{16}H^{12}O^2(C^2H^3O)$, obtained by boiling it for some hours with acetic anhydride and adding alcohol to decompose the excess of acetic anhydride, crystallises from the solution on standing in large well-formed colourless prisms, which after being purified by recrystallisation from alcohol and from petroleum-ether, melt at 103° (Japp, *Chem. Soc. J.* 1879, xxxv. 526).

Reaction with Toluene.—On mixing 5 c.c. of a solution of phenanthraquinone in glacial acetic acid (1 : 200) with 1 c.c. of toluene, adding 4 c.c. of concentrated sulphuric acid, drop by drop, and keeping the liquid cold, a bluish-green colour is produced. When this liquid after a few minutes is poured into water, a turbid purple solution is obtained, from which ether dissolves the colouring matter with a deep reddish-violet colour. This reaction is so sensitive, that even 0.0005 gram of the quinone may be detected by it. On evaporating the ether, a black mass is left behind which in thin layers appears indigo-blue. *Xylene* yields a similar body, dissolving in ether with a cherry-red colour (Laubenheimer, *Ber.* viii. 224).

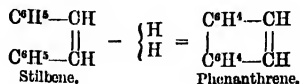
Dibromophenanthraquinone, $C^{14}H^8Br^2O^2$, is produced by heating the quinone to 180° for six hours with the calculated quantity of bromine and a little water, and crystallises from glacial acetic acid in yellow nodules, slightly soluble in alcohol, glacial acetic acid, and benzene, more readily in xylene, melting at 230°. When treated with alkalis, it does not yield an isomeric of alizarin (Hayduck, *Liebig's Annalen*, clxvii. 185). According to Ostermayer (*Ber.* vii. 1090), it melts at 233°, and is converted by oxidation with chromic acid mixture into dibromodiphenic acid, which, as well as the dibromoquinone itself, is but sparingly soluble in all solvents. Its formation is always attended with that of a comparatively small quantity of *tribromophenanthraquinone*, from which it is best separated by means of chloroform.



Phenanthraquinone-carboxylic acid, $C^{14}H^7O^2.COOH = \begin{array}{c} CO.OH.C^6H^4.CO \\ | \\ C^6H^4.CO \end{array}$, produced



by oxidation of phenanthrene-carboxylic acid with chromic acid, is a body having the colour of phenanthraquinone, but distinguished therefrom by its solubility in cold aqueous sodium carbonate, and from phenanthrene-carboxylic acid by its solubility in acid sodium sulphate. It melts at 315° (Japp a. Schultz, *Ber.* x. 1661).

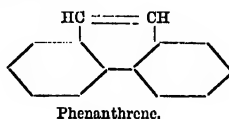
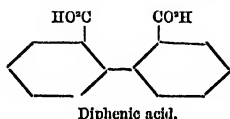
Constitution of Phenanthrene.

The formation of this hydrocarbon from stilbene or symmetrical diphenyl-ethylene (p. 675), by abstraction of hydrogen (vii. 84), shows that it has the constitution of symmetrical diphenylene-ethylene:



Further, G. Schultz (*Ber.* xi. 215) has converted Griess's diamidodiphenic acid, $\text{C}^{14}\text{H}^8(\text{NH}_2)_2\text{O}^4$ (p. 658), on the one hand, into benzidine or diamidodiphenyl, $\text{C}^{12}\text{H}^8(\text{NH}_2)_2$, by heating its barium salt with caustic baryta, and, on the other hand, into diphenic acid, $\text{COOH}.\text{C}^6\text{H}_4-\text{C}^6\text{H}_4.\text{COOH}$, by treating it with dilute nitric acid, converting the resulting nitrate by the action of nitrous acid into the corresponding nitrate of tetrazodiphenic acid, which, when treated with hydriodic acid, yields di-iododiphenic acid, $\text{C}^{12}\text{H}^8\text{I}_2(\text{CO}_2\text{H})_2$, and reducing this latter with sodium-amalgam. Now benzidine is diparadiamidodiphenyl, H_2N   NH_2 , and Griess's diamidodiphenic acid is prepared from meta-amidobenzoic acid, and

must therefore be represented by the formula H_2N   NH_2 , and diphenic acid and phenanthrene by the following formulæ:

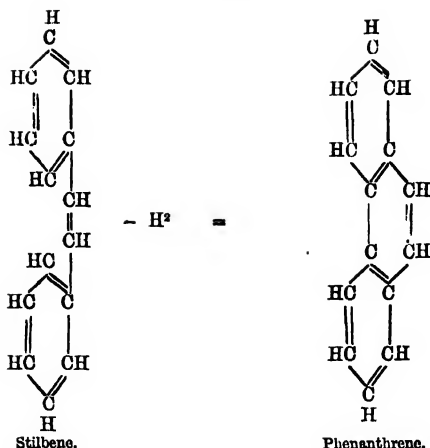


They are therefore di-ortho-compounds, and this conclusion is corroborated by the production of phthalic acid, without admixture of isophthalic or terephthalic acid, by the oxidation of phenanthraquinone by potassium permanganate (p. 1518).

Moreover, as recently pointed out by Japp (*Chem. Soc. J.* 1880, xxxvii. 88), many of the chemical reactions of phenanthrene seem to indicate that the dyad ethylene residue $-\text{CH}=\text{CH}-$ in the diphenylene-ethylene forms part of an aromatic nucleus. On oxidation the two atoms of hydrogen are replaced by two atoms of oxygen (not by one), a quinone being formed. This quinone on reduction yields a quinol (hydroquinone) containing the group $-\text{C}(\text{OH})=\text{C}(\text{OH})-$, and dissolving in caustic alkalis by virtue of these phenylic hydroxyl-groups. Monobromophenanthrene, in which the substitution of bromine takes place in the $-\text{CH}=\text{CH}-$ group—the compound yielding on oxidation phenanthraquinone with elimination of the bromine atom—may, as Anschütz has shown (*Ber.* xi. 1217), be heated with strong alcoholic potash to 170° without undergoing change, and taking into consideration the relative mobility of the bromine-atom in monobromomethylene and monobromostilbene, when these compounds are heated with alcoholic potash, this stability of monobromophenanthrene must be allowed to furnish very strong evidence that the group $-\text{CH}=\text{CH}-$ forms part of an aromatic nucleus.

Further evidence of a similar character may be found in the direct formation from phenanthrene and sulphuric acid of a sulphonic acid, in which the sulphonic group replaces one of the hydrogen atoms of the $-\text{CH}=\text{CH}-$ group (p. 1517). A direct sulphonation of a hydrocarbon has as yet been observed only in the aromatic nucleus. In the fatty series the presence of an electro-negative group (CN , CO_2H , &c.) is necessary, in order that direct sulphonation may take place. All these reactions are specifically aromatic in character, and, taken together, form a strong cumulative proof that the $-\text{CH}=\text{CH}-$ group belongs to a benzene nucleus.

The synthesis of phenanthrene from symmetrical diphenyl-ethylene amounts therefore to the construction of a benzene-nucleus, on the one hand from the ethylene residue $-\text{CH}=\text{CH}-$ (which, as long as it exists in diphenyl-ethylene, shows by its entire behaviour that it does not belong to a benzene-nucleus) and, on the other, from two pairs of carbon-atoms, each of which pairs contained in previously existing benzene-nuclei; thus:



Phenanthrene is therefore diortho-diphenylene-ethylene, and consists of three benzene-nuclei, one of which shares four adjacent carbon-atoms with the two others—one ortho-pair with each. This is the constitution originally attributed to anthracene (vi. 214). According to this view, phenanthrene may be derived from naphthalene by a repetition of the process by which naphthalene is derived from benzene, a suggestion thrown out by Graebe in the memoir above cited (*Liebig's Annalen*, clxvii. 133).

PHENANTHROL, $C^{14}H^9(OH)$. *Hydroxyphenanthrene* (p. 1516).

PHENETHYLAMINE, or *Amido-ethyl-benzene*, $C^6H^5(C^2H^5).NH^2$. A base isomeric with ethyl-aniline, $C^6H^5.NH(C^2H^5)$, and produced therefrom by intramolecular atomic interchange. See BENZENES (ETHYLAMIDO-), (p. 205).

PHENOL, $C^6H^5O = C^6H^5.OH$. This compound is a constant product of the putrefaction of albumin (E. Baumann, *Ber.* x. 685), and is formed, together with indole, when fibrin which has putrefied in contact with the air is subjected for several weeks in closed vessels to the action of water under a layer of ether (Weyl, *Zeitschr. physiol. Chem.* i. 339).

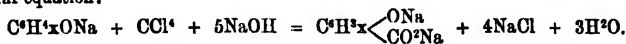
Reactions.—1. Phenol-vapour passed through a red-hot tube is resolved into benzene, toluene, naphthalene, anthracene, phenanthrene, and a liquid boiling between 112° and 145° , which appears to consist for the most part of xylene (Kramers, *Liebig's Annalen*, clxxxix. 129).

2. Phenol, subjected to exhaustive chlorination (p. 1066), is converted into perchlorobenzene, together with perchloromethane, perchlorethane, and carbon dioxide (Ruoff, *Ber.* ix. 1483); by exhaustive bromination in like manner it yields perbromobenzene, together with carbon dioxide (Gessner, *ibid.* 1506).

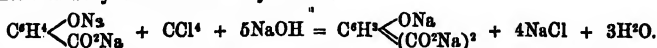
3. By heating with *antimony pentachloride*, it is completely decomposed (Lössner, *J. pr. Chem.* [2], xiii. 418).

4. Heated in a sealed tube at a temperature below 100° with *chromyl chloride*, it yields quinol-ether or quinyloxyde, $(C^6H^4OH)^2O$ (Etard, p. 1444).

5. Phenol heated in an alcoholic solution containing excess of potash or soda with *carbon tetrachloride*, yields a mixture of *ortho*- and *para*-hydroxybenzoic acids (p. 285), and a similar reaction takes place with substituted phenols, according to the general equation:



In this manner chloro-, nitro-, &c. hydroxybenzoic acids may be formed, and similarly phenol-dicarboxylic acid from salicylic acid:



6. With *Alkaline Carbonates*.—Anhydrous phenol, strongly heated for some time in a sealed tube with solid *ammonium carbonate*, yields a colouring matter which dyes silk

and wool a very fine grey, capable of withstanding the action of soap, acids, and light (J. Roth, *Dingl. pol. J.* cxxvi. 560). Phenol fused with *sodium carbonate* yields chiefly catechol, resorcinol, and phloroglucinol, together with small quantities of other substances (Barth a. Schredor, *Ber.* xii. 417). A solution of *potassium carbonate* is decomposed by phenol at the boiling heat (Baumann, *ibid.* x. 686).

6. With *Glycerol*.—When a mixture of 2 pts. phenol, 2 pts. glycerol and 3 pts. sulphuric acid is heated for some time at 120°–130°, the mixture first turns yellow, then yellowish-red, and finally dark red; and on dissolving the thick mass in water, and adding hydrochloric acid, a colouring matter is precipitated which dissolves sparingly in ether, easily in alcohol and in water, but does not appear to be crystallisable. It is coloured a fine red by alkalis, and by salts which have an alkaline reaction, and forms lakes with baryta, alumina, lead oxide, and other metallic oxides. Heated with *aniline*, it forms a red dye-stuff coloured violet-red by ammonia. Similar bodies are obtained from pyrogallol and thymol (C. Reichl, *Ber.* ix. 1429).

7. With *Aniline* and *Sodium Hypochlorite*.—When aniline is added to an alcoholic liquid containing phenol, and then sodium hypochlorite, a brown colour is produced, gradually changing to greenish blue; and on diluting after a while with an equal volume of water, and adding a very small quantity of ammonium sulphide, the colour changes to a pure blue. This colour, which soon turns to brown, is restored by further addition of the hypochlorite (Jacquemin, *Ann. Chim. Phys.* [5], ix. 571). See EUTROPHENIC ACID (p. 738).

8. On the reactions of phenol with *Cinchona-bases*, see pp. 486, 492, 493.

Distinction between Phenol and Creosote.—The following distinguishing characters of phenol and creosote are given by A. M. Read (*Arch. Pharm.* [3], iv. 444):

	<i>Creosote</i>	<i>Phenol</i>
3–4 vols. saturated baryta-water	Turbid solution	Clear solution: after some time slight precipitate or none
Alcoholic solution of ferric chloride	Green	Brown
Aqueous solution of ferric chloride	No reaction	Blue
Glycerin	Soluble; reprecipitated by water	Soluble: not precipitated by water

See also Wätzel (p. 581).

Distinctive tests for Phenol, Cresol, and Creosote are given by H. Allen (*Analyst*, 1878, 319; *Chem. Soc. J.* xxxvi. 182).

Volumetric Estimation.—W. F. Koppeschaar estimates phenol volumetrically by a method, originally suggested by Landolt (*Ber.* iv. 770), founded on the insolubility of tribromophenol. The estimation may be effected by adding a known excess of bromine to phenol, whereby tribromophenol is precipitated, replacing the excess of bromine by iodine, and titrating the latter with sodium thiosulphate. The use of bromine-water is, however, inconvenient in many respects, and it is therefore better to make use of nascent bromine evolved from a mixture of bromide and bromate of sodium. This mixture of salts, $5\text{NaBr} + \text{NaBrO}_3$, is obtained by treating a solution of sodium hydroxide with excess of bromine, evaporating to dryness, and pulverising the residue. Its chemical value must be determined by means of potassium iodide and sodium thiosulphate. To perform the analysis, 25 c.c. of the phenol-solution containing 0.1 g. of the sample are placed in a bottle of 250 c.c. capacity; 100 c.c. of the triturated solution of the mixed salts, and 5 c.c. of strong hydrochloric acid are added, and the bottle, after being closed and shaken, is left at rest for a quarter of an hour, after which it is opened, 10 c.c. of potassium iodide solution are poured in, the bottle is again shaken, and after a while the separated iodine is determined by titration (*Zeitschr. anal. Chem.* 1876, 233; *Chem. Soc. J.* xxxvi. 182).

Phenol-ethers. *Methyl Phenate* or *Anisoil*, $\text{C}^6\text{H}_5\text{O} = \text{C}^6\text{H}_5\text{OCH}_3$.—Some new derivatives of this compound have been obtained by W. H. Perkin (*Chem. Soc. J.* xxxiii. 211).

o-Vinyl-anisoil, $\text{C}^6\text{H}_4\text{CH}=\text{CH}_2$ is prepared by leaving methyl-*o*-oxyphenylacrylic acid (p. 506) in contact with hydriodic acid (sp. gr. 1.94) for two or three days; agitating the mixture frequently, and adding the product by small quantities and with frequent agitation, to a cold aqueous solution of sodium carbonate; boiling the resulting milky liquid in a retort till no more oily product distils over; then warming the distillate to promote the separation of the oil in the form of a layer, and drying this oil

with potassium carbonate. This compound boils between 195° and 200° , but it polymerises so quickly when heated, that its boiling point cannot be determined within narrower limits. When heated for an hour at 150° , it changes into a transparent vitreous polymeride, which is insoluble in alcohol, but dissolves in benzene, and is reconverted into *o*-vinyl-anisole by distillation. In like manner, *ortho*-allyl-anisole, $C^6H^4(OCH^3)C^3H^3$, is obtained from methyl-*o*-oxyphenylcrotonic acid and *ortho*-butenyl-anisole, $C^6H^4(OCH^3)C^4H^7$, from methyl-*o*-oxyphenylangelic acid.

The boiling points and specific gravities of these bodies, and of the corresponding compounds of the *para*-series, are given in the following table:

	Boiling point	Specific gravity		
		at 15°	at 30°	at 45°
Paravinyl-anisole . . .	204° – 205°	1.0029	0.9956	—
Orthovinyl-anisole . . .	uncertain	1.0095	1.0000	—
Parallyl-anisole . . .	232°	—	0.9852	0.9761
Orthoallyl-anisole . . .	222° – 223°	0.9972	0.9884	0.9793
Parabutenyl-anisole . . .	242° – 243°	—	0.9733	—
Orthobutenyl-anisole . . .	232° – 234°	0.9817	0.9740	—

The *para*-compounds crystallise readily; the *ortho*-compounds do not solidify even in a freezing mixture.

Ethyl Phenate or *Phenetoil*, $C^6H^4O = C^6H^3(OC^2H^3)$, is formed by heating a mixture of phenol and ethyl alcohol with zinc chloride, and by heating a solution of phosphoric anhydride in phenol with alcohol (Kastropp, *Ber.* x. 1685). By exhaustive chlorination, it yields perchlorobenzene, together with carbon dioxide and perchlorethane. Methyl phenate, or anisole, similarly treated, yields perchlorobenzene, carbon dioxide, and perchloromethane (Ruoff, *Ber.* ix. 1483).

Nitrophenetols are obtained by the action of sodium ethylate on the corresponding nitrochlorobenzenes, *e.g.*:



It is advisable to use double the quantity of sodium required by the equation, and to add it by small portions. The liquid becomes hot and acquires a red colour; hydrogen is rapidly evolved; and the nitrated phenetoil separates as a brown precipitate, which, after dilution and acidulation, may be collected on a filter, and crystallised several times from boiling alcohol, with addition of animal charcoal. *Trinitrophenetoil* thus obtained crystallises in amber-coloured needles; *dinitrophenetoil* in small yellow needles.

Amidophenols. When *ortho*-amidophenol is treated with bleaching powder, or better with potassium ferricyanide, an amorphous humus-like body is obtained which forms red crystals when heated, and appears to have the composition $C^6H^4N^2O^2$. It is slightly basic, and forms bright-coloured solutions with acids (G. Fischer, *J. pr. Chem.* [2], xix. 317).

Diamidophenols, $C^6H^3(NH^2)^2OH$. (1). *α -Diamidophenol*, $C^6.OH.NH^2.H.NH^2.H^2$, or [1 : 2 : 4]. The hydrochloride of this base is obtained by acting upon *α* -dinitrophenol with tin and hydrochloric acid, and precipitating the resulting tin salt with strong hydrochloric acid. When heated in an oil-bath at 80° – 210° with benzoyl chloride, it yields a di- and a tri-benzoyl derivative.

The *di*-benzoyl-derivative, $C^6H^3(NH.CO.C^6H^5)^2OH$,* is contained in the portion of the crude product which is soluble in alcohol, and may be precipitated from the solution by water. By repeating these operations of solution and precipitation, and finally crystallising the product, best from benzene, it is obtained in crystals having a faint reddish colour and melting at 187° – 188° . It dissolves readily in aniline, alcohols, chloroform, and glacial acetic acid, sparingly in benzene, very sparingly in ether, and not at all in water. Cold fuming nitric acid converts it into *nitrodi*-benzoyl- *α* -diamidophenol, $C^6H^2(NO^2)(OH)(NH.CO.C^6H^5)^2$, which crystallises from glacial acetic acid in slender yellow needles, very slightly soluble in alcohol (K. Stuckenberg, *Ber.* x. 385).

Tribenzoyl- α -diamidophenol, $C^6H^3(OH) \begin{smallmatrix} N(CO.C^6H^5)^2 \\ | \\ NH.CO.C^6H^5 \end{smallmatrix}$, is the chief constituent of the residue left on digesting the product of the above-described reaction in alcohol, and may be extracted therefrom by glacial acetic acid and purified by recrystallisation.

Note by Dr. Armstrong.—Stuckenberg has given no proof that these benzoyl-derivatives have the constitution above indicated. It is more than probable that the H of the OH-group is displaced in the tri-, if not in the di-derivative.

tion. It forms colourless microscopic crystals melting at 231° – 233° , easily soluble in aniline, sparingly in glacial acetic acid, insoluble in alcohol, benzene, ether, chloroform, and water (Stuckenberg).

β -Diamidophenol, $\text{C}^6\text{H}_3(\text{NH}_2)_2$. The hydrochloride, $\text{C}^6\text{H}_3(\text{NH}_2)_2\text{OH}\cdot 2\text{HCl}$, prepared as above described from β -dinitrophenol, [1, 2, 6], is easily soluble in water, sparingly in alcohol, insoluble in ether, soluble in warm dilute hydrochloric acid, from which it crystallises in long rather thick needles. The sulphate, $\text{C}^6\text{H}_3(\text{NH}_2)_2\text{OH}\cdot \text{SO}_4\text{H}_2$, is formed by adding an excess of sulphuric acid to the concentrated solution of the hydrochloride, or by dissolving the latter in dilute sulphuric acid, and separates from the solution on addition of alcohol, in shining needles, light yellow by transmitted light; easily soluble in water, sparingly in alcohol, insoluble in ether. It has not been found possible to obtain any other salts of this base or the base itself.

Benzoyl-derivatives are obtained by treating the hydrochloride with benzoyl chloride at 60° – 195° ; and on digesting the somewhat fluid pulp thereby produced with a solution of sodium carbonate, and filtering, the filtrate deposits a dingy yellow body, and the residue on the filter, when several times dissolved in alcohol, precipitated by water, and finally crystallised from benzene, yields *dibenzoyl- β -diamidophenol*, $\text{C}^6\text{H}_3(\text{NH}\cdot\text{CO}\cdot\text{C}^6\text{H}_5)_2\text{OH}$,* in small prisms having a faint greenish colour, melting at 209° – 213° , easily soluble in alcohol and glacial acetic acid, sparingly in benzene.

The yellow body above mentioned, after being once crystallised from alcohol, may be resolved by chloroform into two compounds, one soluble in that liquid, the other insoluble. The latter consists of *tribenzoyl- β -diamidophenol*, $\text{C}^6\text{H}_3(\text{OH})\cdot \text{N}(\text{CO}\cdot\text{C}^6\text{H}_5)_2\cdot \text{NH}\cdot\text{CO}\cdot\text{C}^6\text{H}_5$ which when purified by crystallisation from alcohol, forms broad needles, melting at 183° – 184° , nearly colourless by reflected light, but exhibiting a rather strong dichroism when examined by the polarising microscope.

Tetrazobenzoyl- β -diamidophenol, $\text{C}^6\text{H}_3[\text{N}(\text{CO}\cdot\text{C}^6\text{H}_5)_2]_2\text{OH}$, is the portion of the yellow body which deliquesces in chloroform. When recrystallised from alcohol it forms thin plates, appearing colourless to brownish yellow by transmitted light, and likewise acting on polarised light, but exhibiting merely alternations of light and darkness. This compound melts at 182° , is insoluble in water, dissolves in alcohol as easily as the preceding, and is more soluble in benzene and in ether.

Triamidophenol, $\text{C}^6\text{H}_3(\text{NH}_2)_3\text{OH}$ (vi. 916). The action of bromine and water on this compound has lately been studied by Weidol & Gruber (*Ber.* x. 1137). The chief product of this reaction is bromodichromazin, $\text{C}^6\text{H}_3\text{N}_3\text{Br}^{11}\text{O}^7$, which is produced by gradually adding bromine (90 c.c.) to a solution of triamidophenol hydrochloride (200 grams) in 50 pts. of water. The blue colour of the diimidoamidophenol first produced then passes into yellow, and on leaving the filtered solution at rest, impure *bromodichromazin* is deposited in glistening brownish-yellow needles; the mother-liquors yield a little more of the substance on agitation with ether. It is purified by washing it with boiling chloroform, and crystallising the residue from alcohol, with the aid of animal charcoal. The long yellow prismatic crystals formed on spontaneous evaporation of the alcoholic solution exhibit a feeble violet dichroism. The compound is very slightly soluble in ether, and insoluble in benzene, chloroform, and carbon bisulphide; boiling alcohol and acetic acid dissolve it with facility. When heated it is decomposed without previous fusion, giving off bromine vapour. It dissolves in concentrated sulphuric acid, but is precipitated by water unchanged, so that it is evidently not a hydrobromide of the compound $\text{C}^6\text{H}_3\text{N}_3\text{Br}^{11}\text{O}^7$.

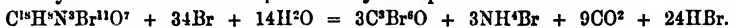
Mercuric acetate, added to a solution of bromodichromazin in acetic acid or alcohol, produces a pale-yellow crystalline precipitate of the compound $(\text{C}^6\text{H}_3\text{N}_3\text{Br}^{11}\text{O}^7)_2\text{Hg} + 3\text{Hg}(\text{C}^2\text{H}_3\text{O}_2)^2$, which, when heated to 100° , becomes brown, evolves bromine, and at a somewhat higher temperature explodes. It is decomposed by sodium-amalgam, with formation of ammonia, and when fused with potassium hydrate yields only oxalic acid.

Bromodichromazin, boiled with a mixture of equal parts of sulphuric acid and water until it no longer separates on dilution, is converted into *bromodichroic acid*, $\text{C}^6\text{H}_3\text{Br}^{11}\text{O}^{11}$, which separates after some time in crystalline crusts, the reaction being $\text{C}^6\text{H}_3\text{Br}^{11}\text{N}_3\text{O}^7 + 4\text{H}^2\text{O} = \text{C}^6\text{H}_3\text{Br}^{11}\text{O}^{11} + 3\text{NH}_3$. A further quantity may be obtained by exhausting the acid liquors with ether. It may be purified by repeated crystallisation from a mixture of ether and benzene with the aid of animal charcoal, and then forms colourless tabular prismatic crystals of considerable size, easily soluble in water, alcohol, and ether. When heated it decomposes below 100° , turning brown, and at a higher temperature evolves bromine, and chars without previous fusion. Its solution has an acid bitter taste, and easily decomposes carbonates. Bromodichroic acid yields

* See note on p. 1522.

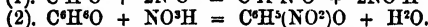
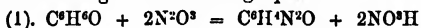
precipitates with lead and silver salts, but they quickly decompose, being transformed into the bromides; alkalis also decompose it very rapidly. The calcium and barium salts are obtained by acting on their respective carbonates with a solution of the acid. They crystallise in slender needles, which are very hygroscopic, and quickly change on contact with the air. Bromodichroic acid is reduced by sodium-amalgam, but the product has not been obtained in the pure state; when fused with potash, it yields acetic acid and resorcinol.

Bromodichromazin boiled for some time with dilute nitric acid, is changed into an oil having the composition of *hexbromacetone*, which crystallises on standing, whilst bromine and bromopierin are produced at the same time. Chromic acid or chromic mixture acts in a similar manner; but an alkaline solution of permanganate completely decomposes the compound. Bromine acts strongly on bromodichromazin suspended in water, causing an evolution of carbonic anhydride, and although the action goes on slowly at the ordinary temperature, it may be completed in a few minutes by heating the mixture at 100°. On cooling, the hexbromacetone above mentioned separates in lustrous scales, which may be purified by crystallisation from chloroform. Its formation by this last reaction is represented by the equation



Hexbromacetone crystallises in monoclinic prisms. It is insoluble in water even at the boiling heat, but dissolves easily in chloroform, carbon sulphide, benzene, and ether, and with partial decomposition in alcohol. It melts in the dry state at 107°–108°, under water at 100°, and decomposes at 200°. By boiling with alkalis, or by heating with water at 180°, it is converted into bromoform. Heated in a sealed tube at 150° with red fuming nitric acid, it is converted into bromopierin; with ammonia it yields bromoform and tribromacetamide. Dissolved in aqueous methyl alcohol and treated with sodium-amalgam, it is converted into pseudopropyl alcohol.

Diazophenol compounds (Weselsky, *Ber.* viii. 895). When nitrous gas is passed into an ethereal solution of phenol cooled with ice, it is quickly absorbed, with formation of diazophenol nitrate together with mono- and dinitrophenol, the reaction taking place according to the following equations:



When the operation is carefully conducted on a rather large scale (200 g. phenol and a litre of ether), the yield of diazophenol nitrate is nearly equal to the theoretical amount. As soon as the nitrous gas ceases to be absorbed, the liquid is left to cool, and after a while needle-shaped crystals are deposited, the formation of which indeed goes on during the absorption of the gas. The liquid separated from them yields on further treatment fresh quantities of the *diazophenol nitrate*, contaminated with resinous products, from which it may be freed by solution in alcohol and precipitation with ether, but even then it retains a faint brownish colour. Diazophenol nitrate is very explosive, but burns without detonation, leaving a large quantity of charcoal. It is decomposed by alkaline liquids, also by boiling with alcohol or with water. The *sulphate*, $\text{C}^6\text{H}^4\text{N}^2\text{O}_4\text{HSO}_4$, prepared by treating the nitrate with 1 vol. sulphuric acid, 2 vols. water, and a small quantity of alcohol, filtering, and mixing the solution with ether till it becomes turbid, crystallises well, is not explosive, and may be dried at 100°. By decomposition with barium chloride, it yields the explosive *hydrochloride*, and from this, or from a mixture of the sulphate with hydrochloric acid, the well-crystallised *platinochloride*, $(\text{C}^6\text{H}^4\text{N}^2\text{OCl})_2\text{PtCl}_6$, may be obtained.

Bromophenols. *Orthobromophenol* has been prepared by Fittig a. Mager (*Ber.* viii. 362) by converting orthobromaniline into diazobromobenzene sulphate and decomposing the latter with water; distilling the product with steam; agitating the distillate with ether; distilling off the greater part of the ether; drying the concentrated ethereal solution with calcium chloride, and distilling it twice. As thus prepared, it is a colourless liquid having a very disagreeable and persistent odour; it boils at 194°–195°, does not solidify on cooling, and is slightly soluble in water. When decomposed by strong potash-ley at the lowest possible temperature, it yields resorcinol as chief product, together with a small quantity of catechol.

Metabromophenol, prepared in like manner from metabromaniline, is a laminar, perfectly colourless mass, which does not alter even in sunshine. Its odour is phenolic, but not nearly so disagreeable as that of the ortho-compound. It melts at 32°–33°, boils at 236°–236.5°, and when pure solidifies in a short time after distillation. The oily compound obtained from metabromaniline by Körner and by Wurster a. Nölting (vii. 905) was impure. Metabromophenol, decomposed with strong potash-ley, yields chiefly resorcinol, together with a small quantity of catechol.

Parabromophenol melts at 64°, not at 66.4° as stated by Körner.

The fact that the three bromophenols, when fused with potash, all yield resorcinol, shows that this compound is the most stable of the three dihydroxybenzenes, and that fusion with potash is by no means a trustworthy method of determining the constitution of an isomeric aromatic compound (Kittig a. Mager).

Tribromophenol, $C^6H_3Br_3$, is converted by the action of potassium sulphite, chiefly into a body which is perhaps a bromo-derivative of $C^{12}H^8O^2$ (Armstrong a. Harrow, *Chem. Soc. J.* xxix. 476). By direct nitration it is converted into orthobrom-*a*-dinitrophenol (m. p. 117°), but by treating 1 mol. tribromophenol dissolved in glacial acetic acid with 1 mol. nitric acid, diorthobromoparanitrophenol, $C^6H_2Br_2NO_2$, is produced (Armstrong a. Harrow, *ibid.* 477). **Tribromophenol bromide**, $C^6H_2Br_3OBr$, is formed by the action of bromine-water in excess on tribromophenol, and is reconverted into the latter by boiling with alcohol or by reduction with tin and hydrochloric acid (Benédikt, *Ber.* xii. 681).

Chlorophenols. **Trichlorophenol**, $C^6H_3Cl_3$, heated at 170° with potassium sulphite, yields the potassium salts of dichlorophenolsulphonic and chlorophenoldisulphonic acids. The former treated with strong nitric acid yields *dichlorororthonitrophenol* melting at 121°; the latter, *diorthonitroparachlorophenol* melting at 80.5° (Armstrong a. Harrow, *loc. cit.*)

Perchlorophenol Chloride, $C^6H_5HO = C^6Cl_5.OH.Cl^2$, is formed by passing an excess of chlorine into an acetic acid solution of metachloracetanilide. The product is precipitated by water, and the precipitate extracted with dilute acetic acid; the insoluble residue is then treated with carbon bisulphide to dissolve the chloride, which crystallises out on evaporation of the bisulphide. By washing with alcohol and recrystallisation from light petroleum, it is obtained in large colourless prisms melting at 78.5°–80°. It is easily soluble in benzene, carbon bisulphide, and alcohol, but only slightly soluble in acetic acid. Alkalis decompose it completely; when heated at 230° with alcohol it yields pentachlorophenol, C^6Cl_5OH , melting at 183° (Beilstein, *Ber.* xi. 2182).

Iodophenols. *Ortho*-iodophenol forms fine crystals melting at 43°. *Para*-iodophenol fused with potash at 165° yields quinol (Körner), but at higher temperatures it yields resorcinol (Nölting a. Wrzesinski, *Ber.* viii. 820).

Cyanophenol, $C^6H^4(CN)O.H$, is formed by boiling diazocyanobenzene nitrate, $C^6H^4(CN)N^2.NO^2$ (vii. 426), with water, filtering the solution after cooling, neutralising the filtrate with ammonia, and evaporating. It is then obtained as a dark-coloured oil which quickly solidifies and may be purified by washing with water, drying, and distillation. It dissolves readily in alcohol and ether, and crystallises therefrom in small white rhombic prisms; from hot water it separates on cooling, also in rhombic prisms. It melts at 82°, has an intensely sweet and at the same time biting taste, and an odour like that of phenol, but fainter. Heated for some hours with strong hydrochloric acid in a sealed tube placed in the water-bath, it is converted into meta-hydroxybenzoic acid (Griess, *Ber.* viii. 859).

Nitrophenols. Determinations of the crystalline form, specific gravity, and solubility of the potassium, barium, and silver salts of the three isomeric mononitrophenols have been made by Post a. Mertens (*Ber.* viii. 1549; *Jahresb. f. Chem.* 1875, 423.)

The action of nitric acid on phenol and the nitrophenols has been studied by Goldstein (*Ber.* xi. 1943) with the following results:

(1). The ratio of the quantity of the more to that of the less volatile of the isomeric nitrophenols, obtained by the action of nitric acid on phenol, bears, within certain limits, a direct proportion to the temperature employed.

(2). By the action of strong nitric acid on *orthonitrophenol*, a crystalline body is formed, which melts at 105°, and dissolves in hot water to an intensely yellow solution having a bitter taste.

(3). A quick method of preparing *dibromonitrophenol* from *orthonitrophenol* consists in adding aqueous bromine to its alkaline solution until no further separation of the product is observed. On filtering, the *dibromonitrophenol* (m. p. 117°) is obtained nearly pure.

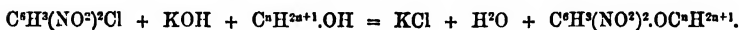
Metanitrophenol, formed from metanitriline by the diazo-reaction, is easily soluble in alcohol and ether, crystallises from carbon sulphide in feathery plates, melts at 96°, and distils unchanged at 194° under a pressure of 70 mm. It decomposes carbonates, forming beautiful salts. The potassium salt crystallises with 2 mol. H^2O , in orange-coloured flat needles.

Metanitransoil is obtained by heating this potassium salt in alcoholic solution with excess of methyl iodide. It crystallises from alcohol in colourless needles, melts at 38°, boils undecomposed at 254°, and is easily volatilised by steam. **Metanitrophenetoil**, prepared in like manner, melts at 34°, boils with slight decomposition at 264° under ordinary pressure, and at 169° under a pressure of 70 mm.

Resorcinol is easily obtained from metanitrophenol through the amido-compound and diazo-reaction. *Trinitroresorcinol* or *Styphnic acid* is formed in theoretical quantity by the long-continued action of boiling concentrated nitric acid on metanitrophenol (A. Bantlin, *Ber.* xi. 2999).

Paranitrophenol.—O. Lehmann (*Zeitschr. f. Kryst.* i. 45) finds that this compound is dimorphous; he distinguishes the ordinary modification by the prefix *b*; the other, which is unstable and produced by the fusion of the first, by the prefix *a*. The *a*-modification is monoclinic. Axes $a : b : c = 0.6796 : 1 : 0.3445$. $\beta = 79.6^\circ$. Combinations $\infty R2$, $+P$, and frequently also $\infty R\infty$. Observed angles: $\infty R2 : \infty R2$ forwards $= 106^\circ 19'$; $+P : +P$ in the vertical edge $= 36^\circ 22'$; $+P : +P$ backwards $= 65^\circ$. Cleavage distinct parallel to $+P\infty$. The first median line forms with the vertical axis an angle of 22° , in the acute angle of the axes *a* and *c*. Through a cleavage-plate parallel to $+P\infty$, both axes may be seen at the edge of the field of view, and situated in the plane of symmetry. The angle of the optic axes is very large. The *b*-modification is also monoclinic, and was formerly regarded by Kokscharow (iv. 396) as identical with the *a*-modification. The first median line for yellow light forms with the principal axis an angle of $47\frac{1}{2}^\circ$ in the obtuse angle of the crystallographic axes. The true angle of the optic axes is 70° , and their plane is parallel to the plane of symmetry.

Dinitrophenols, $C^6H^3(NO^2)^2OH$. Two of these compounds, having the constitutional formulæ $1 : 2 : 4$ and $1 : 2 : 6$ (OH in 1), and designated respectively as the α and β modifications, are described in vii. 909, 910. The following ethers of the α -compound have been examined by Willgerodt (*Ber.* xii. 762), who prepares them by dissolving α -dinitrochlorobenzene, $[Cl : NO^2 : NO^2 = 1 : 2 : 4]$, in the corresponding alcohols, and adding a solution of potash in the same alcohols. The reaction may be represented by the general equation:



Thus by acting on α -dinitrochlorobenzene dissolved in methyl alcohol with a methyl alcohol solution of potash, α -dinitroanisole, $C^6H^3(NO^2)^2.OCH^3$, is obtained. The same compound is formed by the action of a methyl-alcohol solution of potash on an ethereal solution of the dinitro-compound; the reaction may also take place in presence of water. The ether crystallises in long yellow needles melting at 86° – 87° .

α -Dinitrophenetoil, $C^6H^3(NO^2)^2.OC^2H^5$, prepared in a similar manner, substituting ethyl for methyl alcohol, crystallises in long white needles melting at 86° . The corresponding propyl and amyl ethers are yellowish oily liquids.

α -Dinitrophenyl allyl-ether, obtained by acting on α -dinitrochlorobenzene dissolved in allyl alcohol with an alcoholic solution of potash diluted with water, crystallises in long needles or asbestos-like masses, melting at 46° – 47° .

The *glycerol ether*, $C^6H^3(NO^2)^2.OC^3H^7(OH)^2$, is obtained by dissolving dinitrochlorobenzene in glycerol with the aid of heat, and adding to it a solution of potash in glycerol. The product may be crystallised from water, alcohol, or ether; from the latter it separates out as a crystalline mass, melting at 83° .

α -Dinitrophenyl phenyl-ether, $C^6H^3(NO^2)^2.OC^6H^5$, is obtained by acting on a solution of α -dinitrochlorobenzene in carbon bisulphide with potassium phenylate. Crystallised from alcohol it forms long prisms or needles resembling urea-crystals. It melts at 71° . Maikopar (*Ber.* vi. 564) obtained an ether melting at 65° by the action of potash on an alcoholic solution of phenol and dinitrochlorobenzene. This Willgerodt concludes to have been impure, since he has obtained an ether melting at 71° by acting on an alcoholic solution of dinitrochlorobenzene with the calculated quantity of potassium phenylate.

Three other dinitrophenols (γ , δ , ϵ) have been obtained by Bantlin (*loc. cit.*) by the action of nitric acid on metanitrophenol. They are separated by taking advantage of the difference of solubilities of their barium salts in water (δ from γ and ϵ), and in alcohol (γ from ϵ).

γ -Dinitrophenol is soluble in ether and in hot alcohol; is easily volatilised by steam, separating on condensation in yellow needles (m. p. 104°). The potassium salt crystallises with 2 mol. H^2O in thick, bright red needles; the barium salt, with 3 mol. H^2O , in bright red needles.

δ -Dinitrophenol crystallises from water in long colourless silky needles, which melt under water at 50° – 60° , in the dry state at 134° . The potassium salt crystallises from water in red needles; the barium salt with 3 mol. H^2O in red-brown prisms.

ϵ -Dinitrophenol crystallises from water in small yellow needles (m. p. 144°). The

potassium salt crystallises with 2 mol. H_2O in yellow needles; the barium salt crystallises anhydrous in large brown needles.

Dinitroanisols are obtained by heating the potassium salts of the corresponding dinitrophenols with alcohol and methyl iodide at 100° ; also by the action of concentrated nitric acid on metanitroanisole.

γ -*Dinitroanisole* crystallises from alcohol in bright yellow needles melting at 96° ; it boils undecomposed above 360° , and is easily volatilised by steam.

δ -*Dinitroanisole* crystallises in slender golden-yellow needles melting at 70° ; it is less easily volatilised by steam than the γ -compound.

ϵ -*Dinitroanisole* crystallises from alcohol in colourless thick plates melting at 118° .

The three dinitrophenols, γ , δ , and ϵ , are converted by the action of boiling concentrated nitric acid into trinitroresorcinol or styphnic acid, $C^6H(NO_2)_3(OH)_2$ (p. 526).

Constitution of the Dinitrophenols.— α - and β -dinitrophenol are, as already observed, the 1 : 2 : 4 and 1 : 2 : 6 modifications (vii. 908). The constitutional formula of the γ , δ , and ϵ modifications are determined, at least approximately, by the following considerations:

γ -Dinitroanisole, $C^6H(NO_2)_2.OCH^3$, heated in a sealed tube with ammonia at 170° , is converted, like the α - and β -modifications, into a dinitraniline, $C^6H(NO_2)_2.NH^2$, which when treated with ethyl nitrite yields [1 : 3] dinitrobenzene. The δ - and ϵ -modifications, treated in like manner, behave differently, being converted into nitroanisidines or nitro-amido-anisols, $C^6H(NO_2)(NH^2).OCH^3$. The base thus obtained from δ -dinitroanisole, crystallises in brown needles melting at 129° , and subliming without decomposition in light yellow laminae; when treated with ethyl nitrite it is converted into *para*-nitroanisole which volatilises easily with aqueous vapour and melts at 52° .* ϵ -Dinitroanisole, treated in like manner, yields a nitro-anisidine which crystallises in long yellow needles melting at 76° , and is converted by ethyl nitrite into *meta*-nitroanisole.

The relations between these several compounds, and their derivation from meta-nitrophenol, $C^6.OH.H.NO_2.H^3$, may be represented by the following scheme:

γ -Compounds.						
	1	2	3	4	5	6
Dinitrophenol . .	OH	—	NO_2	—	NO_2	—
Dinitro-anisole . .	OCH^3	—	NO_2	—	NO_2	—
Dinitro-aniline . .	NH^2	—	NO_2	—	NO_2	—
<i>m</i> -Dinitrobenzene .	—	—	NO_2	—	NO_2	—
δ -Compounds.						
Dinitrophenol . .	OH	—	NO_2	NO_2	—	—
Dinitroanisole . .	OCH^3	—	NO_2	NO_2	—	—
Nitro-anisidine . .	OCH^3	—	NH^2	NO_2	—	—
Para-nitroanisole .	OCH^3	—	—	NO_2	—	—
ϵ -Compounds.						
Dinitrophenol . .	OH	NO_2	NO_2	—	—	—
Dinitro-anisole . .	OCH^3	NO_2	NO_2	—	—	—
Nitro-anisidine . .	OCH^3	NH^2	NO_2	—	—	—
Meta-nitro-anisole .	OCH^3	—	NO_2	—	—	—

The formation of trinitroresorcinol or styphnic acid from metanitrophenol must be preceded by that of a tetranitrophenol, since styphnic acid may be produced from either of the dinitrophenols above mentioned. This tetranitrophenol has probably, according to Bantlin, the constitution $C^6.OH.NO_2.NO_2.NO_2.NO_2.H$; and as the styphnic acid formed from it must, as a derivative of resorcinol, have its two OH-groups in the meta-position with regard to each other, it may be represented by either of the formulæ $C^6.OH.NO_2.NO_2.NO_2.OH.H$ or $C^6.OH.NO_2.OH.NO_2.NO_2.H$. The former is regarded by Bantlin as the more probable of the two.

* The melting point of this compound is usually given too low. Bantlin finds that when prepared from potassium paranitrophenate and methyl iodide it melts at 52° and boils without decomposition at 274° .

Trinitrophenol or **Picric Acid**, $C^6H^2(NO^2)_3OH$, [1 : 2 : 4 : 6, OH in 1]. On the thermal relations of this compound and its salts, see *HEAT* (pp. 954, 973, 981).

On the explosive force of *Potassium Picrate*, see p. 767.

On the preparation of *Lead Picrate*, and its use for filling percussion-caps, see *Prat* (*Monit. scient.* [3], iv. 665; *Jahresb. f. Chem.* 1874, 1124). This salt is intermediate in explosive power between gunpowder and nitroglycerol.

Ethyl Picrate, $C^6H^2(NO^2)_3OC^2H^5$, which Müller a. Stenhouse obtained by digesting dry silver picrate with ethyl iodide (vi. 911), is also produced by the action of alcoholic potash on an alcoholic solution of picryl chloride, $C^6H^2(NO^2)_3Cl$. The *phenyl-ether* prepared in like manner with an alcoholic solution of potassium phenate, crystallises in white needles (Willgerodt, *Ber.* xii. 1277).

Acetyl Picrate, $C^6H^2(NO^2)_3(OC^2H^3O)$.—When 1 pt. of picric acid and 4 pts. of acetic anhydride are heated in a reflux apparatus for two hours, a yellowish liquid is obtained, consisting of a solution of acetyl picrate in acetic anhydride. On adding water, the picrate is precipitated as a yellowish-white crystalline powder, which is to be washed with water and dried, first by pressure and then in a vacuum. Acetyl picrate melts at $75^\circ-76^\circ$, becoming pale yellow and oily; at 120° it gives off acetic acid; it darkens at 180° , and decomposes completely at 260° . It is soluble in ether, alcohol, and ethyl acetate, also in sulphuric, nitric, and hydrochloric acids. A few hours' exposure to air, and even less when in contact with water, causes it to become yellow, owing to partial decomposition. With an alkali it splits up into picrate and acetate of the alkali-metal. The ethereal solution, when evaporated, deposits beautiful crystals of a deep yellow colour (Tommasi a. David, *Compt. rend.* lxxvii. 207).

Diazobenzene Picrate is formed by the action of diazobenzene nitrate on sodium picrate; also by that of picric acid on diazobenzene-piperidine, $C^6H^2.N^2.NC^2H^4$, dissolved in ether. It forms gold-yellow crystals, which decompose at $95^\circ-100^\circ$; large quantities detonate when heated. It is insoluble in water, alcohol, ether, and benzene (Baeyer a. Jäger, *Ber.* viii. 893).

Isopicric acid, $C^6H^2(NO^2)_3OH$, [1 : 3 : 4 : 5, OH in 1].—This acid is formed by the action of fuming nitric acid on metanitrophenol and on γ and δ dinitrophenols, whence its constitution is established. It crystallises from water, or better from nitric acid, in light yellow, shining, transparent prisms, which melt at 174° , dissolve readily in hot water, with moderate facility in cold water, and colour the skin deep yellow (Bantlin, *Ber.* viii. 21).

Amidonitrophenols, $C^6H^2(NH^2)(NO^2)_2.OH$ (Stuckenberg, *Ber.* x. 382, 385).

α -Amidonitrophenol, [OH : NH^2 : NO^2 = 1 : 2 : 4], is formed by the action of ammonium sulphide on α -dinitrophenol, and best in the following manner. The solution of α -dinitrophenol in a small quantity of alcohol is mixed with a saturated solution of ammonium hydrosulphide till a thin pulp is formed, and into this pulp hydrogen sulphide is passed till the whole has assumed a dark-red colour. The crystalline mass, after filtration, pressing, and drying on bricks, is exhausted with ether, and the filtrate mixed with acetic acid is again filtered, evaporated, and neutralised with strong ammonia. The crystals which separate on cooling are exhausted in the dry state with ether, and the resulting ethereal extract, which contains the α -amidonitrophenol, is mixed with the preceding and left to evaporate. The product may be purified by recrystallisation from boiling water, into which it is introduced in the state of powder, and is thus obtained in orange-coloured hydrated prisms, which melt between 80° and 90° ; the anhydrous compound melts at $142^\circ-143^\circ$.

Benzoyl- α -amidonitrophenol, $C^6H^2(NO^2)_2.NH(COC^6H^5).OH$, formed by the action of benzoyl chloride on the compound just described, may be purified by means of sodium carbonate and recrystallised from aniline. It is insoluble in water, dissolves slowly and with decomposition in alcohol and in glacial acetic acid, easily in aniline, and crystallises in colourless, microscopic, rhombic prisms which melt with decomposition above 200° . *Nitrobenzoyl- α -amidonitrophenol*, $C^6H^2(NO^2)_3.NH(COC^6H^5).OH$, is produced on adding the benzoyl-compound to fuming nitric acid diluted with an equal volume of ordinary strong nitric acid, or better glacial acetic acid, the mixture being kept cool. It crystallises from glacial acetic acid in pale-green prisms melting at $218^\circ-219^\circ$, dissolves sparingly in that liquid, in still smaller quantity in alcohol, and not at all in water. Together with this compound there is formed a secondary product which deliquesces in glacial acetic acid.

Amidodinitrophenol, $C^6H^2(NH^2)(NO^2)_2.OH$, is formed, together with benzoic acid, on heating the benzoyl-derivative just described with hydrochloric acid in a sealed tube at 130° , and may be obtained pure by filtering the product, the benzoic acid then remaining behind; evaporating the filtrate; dissolving the residue in alcohol; precipitating with water; repeating the solution and precipitation several times; and finally crystallising from alcohol. The compound is thus obtained in broad, thick, dark-red

crystals, melting at 169° – 170° , sparingly soluble in ether and in chloroform, easily in warm benzene, glacial acetic acid, water, and strong hydrochloric acid; deliquescent in aniline. From solution in chloroform it separates in monoclinic prisms. From its properties and its reaction with nitrous acid, it appears to be identical with the picramic or nitrophenamic acid which Laurent a. Gerhardt obtained by the action of ammonium sulphide on dinitrophenol (iv. 406).

***β*-Amidonitrophenol**, $[\text{OH} : \text{NH}^2 : \text{NO}^2 = 1 : 2 : 6]$, is prepared, like the *α*-compound, from *β*-dinitrophenol, and purified by dissolving the crude product in alcohol, adding twice the volume of water, and repeating this treatment on the resulting precipitate, till the water which runs away remains clear. It forms red needles, melting at 110° – 111° , dissolving very easily in glacial acetic acid, benzene, ether, and chloroform, easily in alcohol, with moderate facility in boiling water, and with great difficulty in cold water. The *sulphate*, $(\text{C}^6\text{H}^3\text{NH}^2\text{NO}^2\text{OH})^2\text{H}^2\text{SO}^4$, obtained by heating the base with dilute sulphuric acid and precipitating with alcohol, forms colourless laminae, gradually decomposed by water and by alcohol (Stuckenberg).

Bromonitrophenols. The crystalline form of parabromonitrophenol, $[1 : 2 : 4]$ (vi. 915), has been determined by Arzruni (*Zeitschr. f. Kryst.* i. 436). It forms sulphur-yellow monoclinic prisms having the axial ratio $a : b : c = 2.941 : 1 : 1.6249$; $\beta = 64^{\circ} 2'$. Combination $\infty P\infty . \infty P . 0P . -P\infty . +P\infty$, with $-\frac{1}{2}P$ and $+\frac{1}{2}P$ mostly small. The crystals are tabular in the direction of the orthopinacoid. Observed angles, $\infty P : \infty P\infty = 69^{\circ} 17'$; $\infty P\infty : 0P = 64^{\circ} 2'$; $\infty P\infty : -P\infty = 42^{\circ} 14'$. Cleavage imperfect, parallel to $+P\infty$. The plane of the optic axes coincides with the plane of symmetry; the first median line is inclined at about 106° to the axis *c* in the obtuse angle β . Both axes are indistinctly visible in oil in a natural plate having its faces parallel to $\infty P\infty$.

Dibromonitrophenol, $[\text{OH} : \text{NO}^2 : \text{Br} : \text{Br} = 1 : 2 : 4 : 6]$, (p. 915). This compound crystallises in sulphur-yellow monoclinic prisms melting at 117.5° , $a : b : c = 0.5151 : 1 : 0.5912$; $\beta = 65^{\circ} 23'$. Faces $\infty R2$, rarely with ∞P , $0P$, $R\infty$, and in a few crystals also $+P$ and $+2P2$. Observed angles, $\infty R2 : \infty R2 = 86^{\circ} 15'$; $\infty R2 : 0P = 72^{\circ} 18'$; $0P : R\infty = 28^{\circ} 15' 30''$. Cleavage uneven, parallel to $\infty R\infty$ and $0P$. The plane of the optic axes is perpendicular to the plane of symmetry, and nearly perpendicular to the principal axis. The first median line lies in the plane of symmetry, and is very nearly normal to $\infty R\infty$. Apparent angle of axes 70° to 73° for different colours. Dispersion of axes $\rho < \nu$ (Arzruni, *loc. cit.*)

Bromodinitrophenol, $\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)^2\text{OH}$, $[\text{OH} : \text{NO}^2 : \text{Br} : \text{NO}^2 = 1 : 2 : 4 : 6]$, forms yellow monoclinic crystals melting at 85.6° . $a : b : c = 2.7947 : 1 : 1.7783$; $\beta = 67^{\circ} 53'$. Observed forms $P\infty$, $\infty P\infty - P\infty$, $+P\infty$. Measured angles, $P\infty : P\infty = 62^{\circ} 31'$; $P\infty : \infty P\infty = 78^{\circ} 44' - P\infty : \infty P\infty = 42^{\circ} 27'$. The plane of the optic axes coincides with the plane of symmetry; both axes are visible through $-P\infty$. The first median line is inclined at about $57\frac{1}{2}^{\circ}$ to the axis *c* in the obtuse angle β . $2E = 100^{\circ}$ nearly (Arzruni).

Bromiodinitrophenol, $[\text{OH} : \text{NO}^2 : \text{Br} : \text{I} = 1 : 2 : 4 : 6]$, forms monoclinic crystals having the axes $a : b : c = 0.5198 : 1 : 0.5871$; $\beta = 65^{\circ} 32'$. The crystals are dark brown-yellow, melt at 102° , are thickly tabular in the direction of the base, and exhibit, together with the base, which is mostly much rounded, the faces $\infty P\infty$, $P\infty$, ∞P , and $\infty P2$. Observed angles, $\infty P\infty : \infty P2 = 46^{\circ} 35'$; $\infty R\infty : P\infty = 61^{\circ} 53'$; $P\infty : \infty P = 57^{\circ} 42'$. Cleavage imperfect, parallel to $0P$. The plane of the optic axes is perpendicular to the plane of symmetry; the axis *b* is the first median line (P. Groth, *Zeitschr. f. Kryst.* i. 437).

Nitrosophenol, $\text{C}^6\text{H}^4(\text{NO})\text{OH}$ $[1 : 4]$. This compound, discovered by Baeyer a. Caro (vii. 911), has been further examined by E. ter Meer (*Ber.* viii. 622) and by C. Jaeger (*ibid.* 894). The former prepares it by adding nitrosodimethylaniline to boiling dilute soda-ley, cooling the solution quickly, neutralising it with dilute sulphuric acid, and exhausting with ether. The ether is then agitated with dilute ammonia not in excess; the brown ammoniacal solution is saturated with carbonic acid, and shaken with animal charcoal till a filtered sample is precipitated white by an acid; the red-brown filtrate is poured into ice-cold dilute sulphuric acid; and the white or slightly yellowish-green precipitate is drained and dissolved in ether. From the deeply coloured solution thus obtained, the nitrosophenol crystallises, as the ether evaporates, in concentric groups of large laminae, having a faint brownish-green tinge, the yield being equal to 35 to 40 per cent. of the theoretical quantity.

Pure nitrosophenol separates from the hot saturated light green aqueous solution on rapid cooling in small nearly colourless needles; on slow cooling in dendritic groups of laminae having a brownish-green colour. The solution when boiled turns brown, and yields the brown crystals described by Baeyer a. Caro. Nitrosophenol

when pure may be kept without alteration, but when impure it decomposes quickly, turning brown and afterwards black. Ether, acetone, and alcohol dissolve it readily with light green colour. It dissolves less easily in glacial acetic acid, and still less in hydrocarbons. Aqueous alkalis and alkaline earths dissolve it readily with light-brown colour. Acids precipitate it from its solutions as a white amorphous substance.

Sodium-nitrosophenol, $C^6H^4(NO)ONa + 2H^2O$, is obtained by adding 1 pt. of sodium dissolved in alcohol to a cold ethereal solution of 7 pts. nitrosophenol, washing the minium-coloured amorphous precipitate with ether, and drying it in a vacuum. From alcohol and acetone it crystallises in short red needles. Water dissolves it very easily with red colour; the alcoholic solution is red-brown in thick layers, yellow-green in thin layers; the solution in acetone is blue-green. It does not dissolve in ether or in hydrocarbons. When exposed to the air in contact with ether, it becomes dark-red and crystalline on the surface. It is permanent in the dry state at ordinary temperatures, but detonates when heated. Its solutions are not decomposed by boiling, but on adding an acid (not carbonic acid), nitrosophenol separates out. *Potassium-nitrosophenol* is obtained by precipitation as an amorphous substance, becoming red and crystalline when moist. From alcohol or acetone it crystallises in thin blue-green tablets, sometimes also in red crystals. *Ammonium-nitrosophenol* is a green unstable salt. *Barium-nitrosophenol*, $[C^6H^4(NO)O]^+Ba$, is prepared by adding a concentrated solution of 10 pts. barium hydrate to an alcoholic solution of 8 pts. nitrosophenol, precipitating with ether, mixing the saline solution which separates with alcohol, and again precipitating with ether. By a repetition of this treatment, a red crystalline precipitate is obtained, which, when dried at 100° , has the composition above given. It is easily soluble in water, and crystallises therefrom in large red needles. *Silver-nitrosophenol*, $C^6H^4(NO)OAg.H^2O$, is formed on adding an aqueous solution of 1 pt. silver nitrate to a solution of 1 pt. of the sodium salt in 600 pts. of hot water, and separates after a short time in blackish-violet crystals having a green reflex and appearing red by transmitted light under the microscope. The other metallic salts of nitrosophenol may be obtained in like manner as amorphous or crystalline dark-coloured precipitates. Ethers have not been obtained; but the action of methyl iodide on the alkali-salts gives rise to well-crystallised products (ter Meer). R. Lex (*Ber.* iii. 457) observed that when an aqueous solution of nitrosophenol is mixed with a nitrite and then supersaturated with soda, a dark-brown solution is formed, which by certain reducing agents (warming with sugar, aluminium, or zinc) is rendered lighter, and, if then exposed to the air or left in contact with a hypochlorite, assumes a deep blue colour. According to ter Meer, however, this reaction does not take place with nitrosophenol alone, but requires also an excess of phenol; with pure nitrosophenol only a brown colour is obtained.

The following reactions of nitrosophenol have been observed by C. Jaeger (*Ber.* viii. 894). When nitrous gas is passed into an ethereal solution of nitrosophenol, the latter is converted into Weselsky's diazophenol nitrate (p. 1524), which when heated with phthalic anhydride yields quinzarin, while small quantities of the three nitrophenols remain in the mother-liquor.

When nitrosophenol is treated with strong hydrochloric acid, an energetic reaction takes place, and amorphous products are formed, but when a stream of gaseous hydrogen chloride is passed into a cooled ethereal solution of nitrosophenol, brownish needles separate, consisting of a *dichloramidophenol*, soluble in acids and in alkalis, slightly soluble in water, non-volatile with water-vapour, melting at 175° , not distilling without decomposition. Chlorophenol is obtained at the same time by a secondary reaction.

When finely pounded nitrosophenol, cooled with ice, is treated with a solution of hydrochloric acid in methyl alcohol, a brownish solution is obtained, which deposits fine needles, consisting principally of the hydrochloride of a solid base, which passes over, together with a small proportion of a basic oil and chlorophenol, when the crystals are distilled with water. This base is *methyldichloramidophenol*; it melts at 71.5° , separates from dilute alcohol in long needles, and differs from the non-methylated base by being volatile with water-vapour, and insoluble in alkalis.

When the methyl-alcohol used in the above experiment is replaced by ethyl-alcohol, an *ethylated dichloramidophenol* or *dichloramidophenetol* is obtained, which separates from dilute alcohol in splendid long colourless needles, melting at 46° , distilling at 275° , and volatilising readily at 100° , or with water-vapour. Its *hydrochloride* and *platinum salt* form needles, and most of its salts are partially decomposed by water.

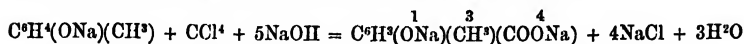
When nitrosophenol is dissolved in excess of strong potash-ley, the solution evaporated and heated for some time at 180° , the melt dissolved in water, and the brown aqueous solution treated with hydrochloric acid, a precipitate is obtained consisting of azophenol, which may be purified by repeated crystallisation from dilute alcohol. It melts at 214° , dissolves readily in alcohol and alkalis, sparingly in ether

and in hot water, scarcely at all in benzene. Though stable for the most part, it cannot be sublimed without decomposition (Jaeger).

On the formation of Oxyazobenzene, $C^{12}H^{10}N^2O$ (vii. 151), and Azophenin, $C^8H^8N^2O$, by the action of nitrosophenol on aniline acetate, see AZOPHENIN (p. 138).

Phenol-carboxylic or Hydroxybenzene-carboxylic Acids. The phenol-monocarboxylic acids, $C^6H^3(OH).COOH$, are identical with the three hydroxybenzoic acids (pp. 278-287 and 1459-1463).

Hydroxybenzene-ortho-dicarboxylic, Hydroxy-ortho-phthalic, or simply **Hydroxyphthalic Acid**, $[OH : CO^2H : CO^2H = 1 : 3 : 4]$. This acid is produced by the following series of reactions: 1. Metacresol, $C^9H^4(OH)(CH^3)$, heated in strongly alkaline solution with carbon tetrachloride, is converted into a salt of meta-methyl para-hydroxybenzoic or $[1 : 3 : 4]$ hydroxytoluic acid:



2. This sodium salt treated with methyl iodide yields the methylic ether of the corresponding methoxytoluic acid, $C^6H^3(OCH^3)(CH^3)(CO^2CH^3)$. 3. This acid oxidised with

potassium permanganate yields methoxy-orthophthalic acid $C^6H^2(OCH^3)(CO^2H)(CO^2H)$, which crystallises in stellate groups of needles melting at $138^\circ-144^\circ$; and 4. The methoxy-acid is converted by heating with hydrochloric acid under pressure, or by fusion with potash, into hydroxyorthophthalic acid, $C^6OH.H.CO^2H.CO^2H.H^2$ (C. Schall, *Ber.* xii. 816).

The same acid is formed as an ethyl-salt, by the action of nitrous acid on ethyl amidophthalate. The amido-ether is dissolved in 10 pts. of dilute sulphuric acid (1 : 5); the solution is clarified with animal charcoal; a quantity of solution of sodium nitrite, not quite sufficient for complete decomposition, is added by small portions; and the mixture is heated to 100° . The ethyl hydroxyphthalate then separates as a yellowish, mobile, uncrystallisable oil which cannot be volatilised without decomposition. It may be saponified by boiling with strong potash-ley, and the resulting solution yields, with normal or basic acetate of lead, a precipitate of lead hydroxyphthalate, from which the hydroxyphthalic acid may be separated by hydrogen sulphide, and obtained by extraction with ether and evaporation, as a crystalline mass of microscopic plates. For purification, it is converted into the anhydride (*infra*), the solution of which in hot water deposits the acid on cooling in rosettes of short spicular crystals (Bayer, *Ber.* x. 124, 1079).

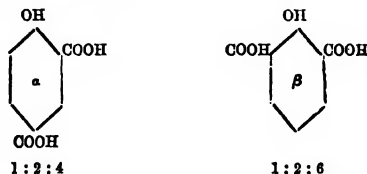
Hydroxyphthalic acid dissolves very easily in hot water and in 32.4 pts. of water at 10° . It is very soluble in alcohol and acetone, less so in ether; dissolves easily in glacial acetic acid on heating; hydrocarbons dissolve only traces of it. At about 180° it melts and is partially resolved into water and the anhydride. The hydroxyphthalates of the alkalis and the alkaline earths are very soluble. The ammonium salt crystallises well, and its solution forms with lead acetate a white amorphous precipitate; with silver nitrate a white precipitate of the silver salt, $C^6H^4Ag^2O^4$, consisting of tufts of needles slightly soluble in water. The aqueous solution of the acid gives a red colour with ferric chloride.

Fuming nitric acid converts hydroxyphthalic acid into a nitro-product; nitrous acid turns it yellow on heating. Dilute sulphuric acid (1 : 2 and 1 : 4) does not alter it even after six hours' heating at $160^\circ-180^\circ$; the strong acid dissolves it without colour at ordinary temperatures, with brown coloration and evolution of gas at 180° . When hydroxyphthalic acid is heated with 16 pts. of strong sulphuric acid for four hours at 200° , and the resulting solution is mixed with water, a dingy greenish-yellow precipitate is formed, from which ether extracts at least three substances, viz.: 1. A yellow sublimable body resembling anthraflavone. 2. A substance resembling phenolphthalidein, and forming, with strong sulphuric acid, a solution which has a splendid red colour and exhibits three absorption-bands. 3. A colourless substance which melts at 120° , sublimes without alteration, dissolves in strong sulphuric acid without colour, and in melting potash with yellowish colour. Hydroxyphthalic acid in aqueous solution is easily reduced by sodium-amalgam.

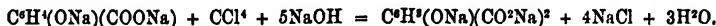
Hydroxyphthalic anhydride, $C^6H^4O^4 = C^6H^3OH(CO)^2O$, is best prepared in large quantity by heating the acid at 210° in a retort through which a slow stream of dry air is passing. It melts at $165^\circ-166^\circ$, sublimes at $200^\circ-210^\circ$ in feathery groups of long needles, and may be distilled in small quantities without decomposition. It dissolves slowly in cold water, quickly in hot water, reproducing the acid; easily in methyl alcohol, ethyl alcohol, acetone, and ether, but is nearly insoluble in benzene, chloroform, and carbon sulphide. With aniline at $160^\circ-180^\circ$, it forms a crystalline anilide.

With *phenols*, hydroxyphthalic anhydride forms hydroxyphthaleins, compounds which exactly resemble the corresponding phthaleins, with the exception of slight differences of colour, their coloured salts generally exhibiting a more decided red colour than those of the phthaleins. This reaction affords a means of distinguishing hydroxyphthalic acid from hydroxyiso- and hydroxyterephthalic acids. See *PHTHALEINS*.

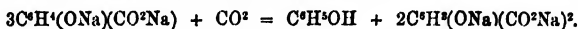
2. Hydroxybenzene-*m*-dicarboxylic or Hydroxyisophthalic Acids. Two of these acids, distinguished as α and β , are known, their constitution being represented by the following formulæ:



They are obtained: (a). By fusing the three aldehydo-hydroxybenzoic acids $C^6H^4(OH)(COH)(COOH)$, already described (pp. 288, 1463), with potassium hydroxide the β -acid being thus produced from orthoaldehydosalicylic acid, $[OH : COH : COOH = 1 : 2 : 6]$, and the α -acid either from para-aldehydosalicylic acid, $[OH : COOH : COH = 1 : 2 : 4]$, or from orthoaldehydo-parahydroxybenzoic acid, $[OH : COH : COOH = 1 : 2 : 4]$ (Tiemann & Reimer, *Ber.* x. 1562). (b). By the action of carbon tetrachloride and a caustic alkali (Reimer & Tiemann's reaction) on salicylate of potassium or sodium:

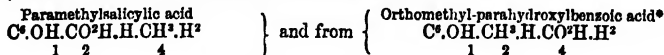


The solution of the salicylate in an aqueous alkali is mixed with a quantity of alcohol sufficient to dissolve nearly the whole of the carbon tetrachloride, and the mixture is somewhat strongly heated in a sealed tube till an abundant separation of potassium or sodium chloride takes place. Both the α - and β -acids are obtained by this process, the α -acid being, however, by far the more abundant. The two acids are separated by converting them into their barium salts, that of the α -acid being the more soluble of the two (G. Hasse, *Ber.* x. 2185). (c). The α -acid is produced—together with phenol-tricarboxylic acid and phenol—by heating the disodic salt of salicylic or parahydroxybenzoic acid in a stream of carbon dioxide:



The same result may also be obtained by heating sodium phenate, or better a mixture of the phenates of potassium and sodium, in a stream of carbon dioxide, a salt of salicylic acid being first produced, and afterwards converted into the hydroxyisophthalate. The best result is obtained by using 3 mol. sodium phenate to 1 mol. potassium phenate, and passing the gas over the mixture first at 120° – 130° , then for some time (two hours with 50 grams of phenol) at 300° – 320° . 50 grams of phenol yield by this process 10 to 20 grams of pure hydroxy-isophthalic acid (Ost, *J. pr. Chem.* [2], xiv. 93; xv. 301).

(d) α -Hydroxyisophthalic acid is also produced from



by a series of transformations exactly analogous to those just described for the formation of hydroxy-orthophthalic acid from metamethyl-parahydroxybenzoic acid.

α -Hydroxyisophthalic acid, when pure, crystallises in needles, dissolves easily in alcohol and ether, and in 5000 pts. of water at 10° . According to Tiemann & Reimer (*Ber.* x. 1562), it dissolves in 145 pts. water at 100° , and in 300 pts. of water at 24° . It resembles salicylic acid in general appearance; produces a deep reddish-violet coloration with ferric chloride; melts at 270° – 280° (Tiemann & Reimer); above 300° (Schall), and sublimes with partial decomposition. The acid is a bi-basic hydroxyacid, and is, therefore, capable of forming three series of salts, normal, acid, and so-called basic salts, that is, salts in which the phenolic as well as the carboxylic hydrogen is replaced by metals. The normal salts are formed by neutralising the acid with carbonates.

* On the preparation of these and the other acids of the formula $C^6H^4(OH)(CH_3)(CO^2H)$, see page 1540; also *TOLUIC ACIDS, HYDROXY-*.

The *sodium salt*, $C^6H^3(OH)(COONa)^2 + aq.$, crystallises in long needles, which retain 2 mols. of water when dried in the air, and dissolve easily in water. The *potassium, ammonium, barium, calcium, zinc, manganese, cobalt, nickel, and cadmium salts* are all soluble in water. The sodium salt, when heated to $220^\circ-250^\circ$, decomposes in the same manner as normal sodium salicylate, yielding the basic salt, phenol, and carbon dioxide:

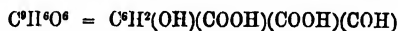


The *normal silver salt*, $C^6H^3(OH)(COOAg)^2$, obtained by precipitating the ammonium salt with silver nitrate, is amorphous and nearly insoluble in water. The *acid silver salt*, $C^6H^3(OH)COOH.CO_2Ag$, is formed by adding to the free acid an excess of silver nitrate. It crystallises in needles, which dissolve in water. The *basic calcium salt*, $C^6H^3O_2Ca(COO)_2Ca^2 + 5H_2O$, obtained by adding lime-water to a solution of the normal salt, is sparingly soluble in water.

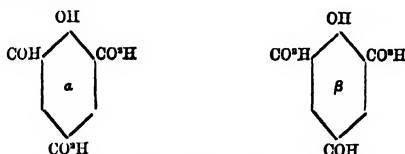
The *ethylic ether*, $C^6H^3(OH)(COOC^2H_5)^2$, obtained by passing hydrogen chloride into an alcoholic solution of the acid, distils with steam in snow-white crystals which melt at 52° (Ost).

β . Hydroxyisophthalic acid is also produced from orthomethylsalicylic acid, $C^6H^3.OH.CH^1.CO^2H$, by a series of transformations analogous to those described for the preceding modification (Schall, *loc. cit.*) It crystallises from water in capillary needles, or sometimes in well-defined prisms, having the composition $C^6H^4O^5 + H_2O$; dissolves in 35 to 40 pts. water at 100° , and in 700 pts. at 24° , easily in alcohol and ether, less easily in chloroform. In the air-dried state it melts at 239° ; after drying over the water-bath, at $243^\circ-244^\circ$. It can only be partially sublimed without decomposition. The aqueous and alcoholic solutions exhibit a blue-violet fluorescence which disappears on addition of excess of alkali. The aqueous solution gives a cherry-red colour with ferric chloride. The acid reddens litmus, the solution turning blue again on addition of a quantity of alkali sufficient to form a normal or bi-metallic salt. The *potassium, sodium, and ammonium salts* are very soluble. The characters of the other salts are exhibited in the table on p. 1536, which gives a comparative view of the reactions of α - and β -hydroxyisophthalic or hydroxybenzene-metadicarboxylic acid, also of those of phenol-tricarboxylic or hydroxytrimesic acid (Tiemann u. Reimer, *Ber.* x. 1562).

Aldehyde-hydroxyisophthalic acids, or *Formyl-hydroxyisophthalic acids*,



(Reimer, *Ber.* xi. 793). Two of these acids, α and β , are known, and are represented by the following formulæ:



They are formed by the action of chloroform in alkaline solution on α - and β -hydroxyisophthalic acids respectively, the mode of action being similar to that by which the aldehyde-hydroxybenzoic acids are formed from salicylic and parahydroxybenzoic acids (p. 288). α -Hydroxyisophthalic acid thus treated yields a mixture of *aldehyde- α -hydroxyisophthalic* and *para-aldehydosalicylic acids*, which may be separated by treating the ethereal extract of the crude product with solution of acid sodium sulphite, boiling the compound thus formed with sulphuric acid to set free the two aldehyde-acids; then dissolving them in ammonia; adding sal-ammoniac and magnesium sulphate; and leaving the mixture at rest for a day or two. The magnesium salt of the aldehyde- α -hydroxyisophthalic acid is then deposited in crystalline form, and the aldehyde-acid separated from it, crystallises from water in felted needles which melt with decomposition at 260° . It is very soluble in boiling water, less soluble in cold water, easily soluble in alcohol and ether. Its solution is coloured blood-red by ferric chloride. Like the other ortho-aldehydehydroxybenzoic acids, it forms colourless neutral solutions and yellow alkaline solutions, both exhibiting a green fluorescence. In the neutral solutions, calcium and magnesium salts form no precipitates; barium chloride, a crystalline precipitate after some time from cold solutions, more quickly on warming; ferric chloride, a dark-red coloration, and a flocculent precipitate on warming; silver nitrate, a gelatinous precipitate which when dried

over sulphuric acid has the composition $C^6H^4Ag^2O^4 + H^2O$, and gives off its water at 100° . The solution of the free acid gives with silver nitrate a crystalline acid silver salt easily soluble in hot water. The basic or trimetallic salts, except those of the alkali-metals, are for the most part sparingly soluble. The basic cupric salt, like that of ortho-aldehydo-salicylic acid, dissolves, when recently precipitated, in excess of ammonia, but is reprecipitated on heating, and is then nearly insoluble in ammonia.

Aldehydo- β -hydroxyisophthalic acid, $C^6H^1.OH.CO^2OH.H.CO^4H.H.CO^6OH$, is the only product of the action of chloroform and alkalis on β -hydroxyisophthalic acid. It crystallises in tufts of long slender needles which melt, with decomposition, at 237° – 238° . When dried at 100° it contains $\frac{1}{2}H^2O$. In crystalline form, melting point, solubility, reaction with ferric chloride, and fluorescence, it closely resembles β -hydroxyisophthalic acid. From solution in sulphuric acid, it is precipitated by water in the form of a crystalline pulp (β -hydroxyisophthalic acid is not thus precipitated). Its alkaline solutions are colourless. Amongst its normal (bi-metallic) salts, those of calcium and magnesium are easily soluble, that of barium is sparingly soluble in water. The normal silver salt is moderately soluble in hot water, and crystallises on cooling; its ammoniacal solution does not blacken when heated. The neutralised solution of the acid is coloured dark-red by ferric chloride. The solution of the free acid is not precipitated by silver nitrate. Its ammoniacal solution gives a precipitate with barium chloride, none with calcium chloride or magnesium sulphate. Cupric sulphate added to the slightly ammoniacal solution, forms a green precipitate, which dissolves easily in ammonia.

The aldehydo-hydroxyisophthalic acids cannot be oxidised by fusion with potash, as they are decomposed thereby, with separation of carbon dioxide. When oxidised by potassium permanganate in cold alkaline solution, they both yield a small quantity of phenol-tricarboxylic or hydroxytrimesic acid, identical with that which Ost obtained, together with the two phenol-dicarboxylic acids, by heating disodic salicylate in a stream of carbon dioxide (p. 1532).

3. Hydroxybenzene- p -dicarboxylic or Hydroxyterephthalic Acid, is obtained: (a) By dissolving crystallised amidoterephthalic acid in soda-ley, acidifying the solution with sulphuric acid, adding the requisite quantity of potassium nitrite in aqueous solution, and boiling. It forms a white powder easily soluble in methyl and ethyl alcohols, sparingly in water; melts above 300° , and sublimes with partial decomposition at a higher temperature. Mixed with sand and subjected to dry distillation, it is resolved into carbon dioxide and phenol, and by prolonged heating with hydrochloric acid at 120° into carbon dioxide and methahydroxybenzoic acid. Its aqueous solution gives with ferric chloride a deep violet-red coloration, resembling that produced by salicylic acid. (b) From meta-methylsalicylic acid, $C^6H^1(OH)(CO^2H)(CH^5H^3)$, or from ortho-methyl-meta-hydroxybenzoic acid, $C^6H^1(OH)(CH^2)(CO^5H)$, by a series of processes analogous to those employed in the preceding cases (Schall).

The *silver salt*, $C^6H^1(OH)(COOAg)^2$, is white and insoluble in water. The *barium salt*, $C^6H^1.OH.(COO)^2Ba + Aq.$, crystallises from water in white laminae.

Dimethyl hydroxyterephthalate, $C^6H^1(OH)(COOCH^3)^2$, obtained by passing hydrogen chloride into a solution of the acid in methyl alcohol, crystallises from methyl alcohol in beautiful silky needles, which melt at 94° . It dissolves in hot water, and easily in aqueous alkalis, alcohol, and ether. The solution in ammonia gives precipitates with salts of the heavy metals.

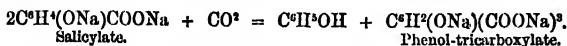
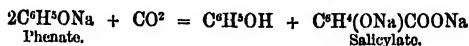
Dimethyl acetoxysterephthalate, $C^6H^1\left\{ \begin{matrix} OC^2H^3O \\ (CO^2CH^3)^2 \end{matrix} \right\}$, obtained by heating the dimethyl-ether to 100° with excess of acetyl chloride in sealed tubes, crystallises from alcohol in white, cauliflower-like masses, melting at 76° . It is insoluble in soda-ley (G. A. Burkhardt, *Ber.* x. 144).

Dinitro-hydroxyterephthalic acid, $C^6H(NO^2)^2(OH)(COOH)^2$, is obtained by treating hydroxyterephthalic acid with a mixture of fuming nitric and Nordhausen sulphuric acids, and crystallises from cold water in fine golden-yellow transparent crystals, dissolving easily in cold water, and melting at 178° . No isomeric acid is formed. The dinitro-acid and its salts are explosive.

The *acid silver salt*, $C^6H(NO^2)^2OH(COOK)COOAg$, formed on mixing concentrated solutions of the acid and of silver nitrate, is a yellow crystalline powder, moderately soluble in water. The *normal silver salt*, $C^6H(NO^2)^2OH(COOAg)^2$, is obtained by triturating a concentrated solution of the acid with moist silver oxide, and evaporating the filtrate over sulphuric acid. It forms blood-red prismatic crystals, very easily

soluble in water; crystallises from aqueous solution with 2 mols. of water. The *acid lead salt*, $C^6H(NO_2^3)OH(COOH)COOpb$ ($pb = 103.5$), formed on adding neutral lead acetate to a solution of the acid, is a yellow crystalline powder, sparingly soluble in water. The *neutral calcium salt*, $C^6H(NO_2^3)OH(COO)^2Ca$, formed by boiling a solution of the acid with calcium carbonate, is yellow and crystalline, and dissolves sparingly in water (Burkhardt, *Ber.* x, 1273).

Phenol-tricarboxylic Acid, $C^6H^3O^7 = C^6H^2(OH)(COOH)^3$ (Ost, *J. pr. Chem.* [2], xiv. 93; xv. 301). This acid is formed, together with α -hydroxybenzene-*m*-dicarboxylic or α -hydroxyisophthalic acid, by heating disodic salicylate in a stream of carbon dioxide at a temperature above 300° . It is not however necessary to make use of ready-prepared sodium salicylate; a better mode of proceeding is to start from sodium phenate, the process being first conducted in the manner already described for the preparation of salicylic acid (vii. 1065), and the temperature being afterwards raised to 370° – 380° . The reaction takes place by two stages, as represented by the following equations:



The yield amounts to nearly the theoretical quantity, viz. three-fourths of the phenol employed.

Phenoltricarboxylic acid crystallises from alcohol in needles, and from water in prisms containing 1 mol. or needles containing 2 mols. of water. It dissolves freely in alcohol, sparingly in ether, and in 200 pts. of water at 10° . It produces a deep red coloration with ferric chloride. When heated it undergoes complete decomposition, yielding chiefly phenoldicarboxylic acid and carbon dioxide, with a little salicylic acid and phenol. Being a tribasic acid, and containing the hydroxyl-group of phenol, it is capable of forming four series of salts. The normal salts of the alkalis are crystallisable and easily soluble in water. All the other salts are either insoluble or but sparingly soluble.

The *normal barium salt*, $[C^6H^2(OH)(COO)^3]^2Ba^3 + 8H^2O$, and the corresponding *calcium salt*, obtained by double decomposition, are very sparingly soluble in water.

The *normal silver salt*, $C^6H^2(OH)(COOAg)^3 + 3H^2O$, is a crystalline precipitate.

The *di-acid calcium salt*, $[C^6H^2(OH)(COOH)^2COO]^2Ca + 6H^2O$, and the corresponding barium salt, are formed by mixing solutions of the free acid with calcium or barium chloride; they are crystalline and soluble in water. The other acid phenoltricarboxylates are likewise soluble in hot water, and crystallise on cooling, the potassium and ammonium salts in slender needles.

Ethyl phenoltricarboxylate, $C^6H^2(OH)(COOC^2H^5)^3$, is readily formed by passing hydrogen chloride into an alcoholic solution of the acid. It crystallises from a hot alcoholic solution in long colourless prisms, which melt at 84° , and sublime with partial decomposition at a higher temperature. When boiled with aqueous soda it is slowly decomposed, yielding phenoltricarboxylic acid, but when it is digested with soda in the cold, the hydrogen of the hydroxyl-group is replaced by sodium, whereby the following compound is formed.

Ethyl-sodium phenoltricarboxylate, $C^6H^2(ONa)(COOC^2H^5)^3$.—This body is best obtained by dissolving the foregoing ether in absolute alcohol and adding alcoholic soda, whereupon it crystallises in large oblique prisms. It is insoluble in water, cold alcohol, and ether. When boiled with water for some time, it gradually dissolves, forming a solution which on cooling deposits needles of *sodium diethylphenoltricarboxylate*, $C^6H^2(OH)(COOC^2H^5)^2COONa$, which crystallises from alcohol with 1 mol. of water. Its aqueous solution, which is neutral, gives precipitates with salts of barium, silver, and other metals.

Diethylphenoltricarboxylic acid, $C^6H^2(OH)(COOC^2H^5)^2COOH$, is precipitated on saturating an aqueous solution of the foregoing salt with hydrogen chloride. It crystallises from alcohol in long needles containing 1 mol. of water. The anhydrous substance melts at 118° .

Phenoltricarboxylic acid heated in a reflux apparatus for several hours with 4 mols. phosphorus pentachloride, is converted into chlorotrimelic acid, $C^6H^2Cl(COOH)^3$, which when reduced with zinc and a dilute acid, or better with sodium-amalgam, is converted into trimelic acid, $C^6H^3(COOH)^3$, [1 : 3 : 5]: hence

Reactions of Phenol-carboxylic Acids.

Reagents	α -Phenol-dicarboxylic or α -Hydroxy-isophthalic acid		β -Phenol-dicarboxylic or β -Hydroxy-isophthalic acid		Phenol-tricarboxylic or Hydroxy-trimesic acid	
	Neutral solution	Ammoniacal solution	Neutral solution	Ammoniacal solution	Neutral solution	Ammoniacal solution
Calcium Chloride.	—	A basic calcium salt separates after long standing, more quickly when heated.	A calcium salt crystallising in stellate groups of needles separates after some time. Crystalline barium salt separates on heating.	A white bulky basic calcium salt is quickly precipitated.	White calcium salt becoming crystalline when heated.	White bulky precipitate.
Barium Chloride.	—	—	—	Precipitation of basic barium salt at ordinary temperature. No precipitation in presence of sal-ammoniac.	Immediate precipitation of white barium salt.	The same.
Magnesium Sulphate	—	No precipitation in presence of sal-ammoniac.	—	—	After long standing, more quickly on heating, or on rubbing with a glass rod, a magnesium salt separates in fine needles.	The same.
Silver Nitrate	White crystalline silver salt nearly insoluble in boiling water. A solution strongly acidulated with acetic acid deposits an acid silver salt soluble in hot water.	The normal silver salt dissolves easily in excess of ammonia.	White crystalline lead-salt easily soluble in acetic acid. In a solution strongly acidulated with acetic acid, no precipitation takes place.	Behave like α -Phenol-dicarboxylic acid.		
Lead acetate	—	Bulky white basic lead salt.	White crystalline lead salt only slightly soluble in acetic acid. From a solution acidulated with acetic acid, an acid lead salt is precipitated, which may be recrystallised from boiling water.	Bulky white basic lead salt.	White crystalline lead salt, not completely soluble in acetic acid. From a solution acidulated with acetic acid, lead salts are precipitated, which dissolve but sparingly even in boiling water.	Bulky white basic lead salt.

it follows that phenoltricarboxylic acid has the constitution of hydroxy-trimesic acid, $C^6H^3O^3H.OH.CO^2H.H.CO^2H.H$.

The table on page 1536 exhibits a comparative view of the reactions of the two phenol-meta-dicarboxylic acids and of phenoltricarboxylic acid with various saline solutions.

Phenol-diazobenzene, $C^{12}H^{10}N^2O = C^6H^5O.C^6H^4N^2$, and **Phenol-didiazobenzene**, $C^{18}H^{14}N^4O = C^6H^5O.2C^6H^4N^2$. These compounds, discovered by Griess, were originally produced by the action of barium carbonate on a cold aqueous solution of diazobenzene nitrate (see iv. 433, where they are designated as phenates of azophenylamine and diazophenylamine respectively).

Phenol-diazobenzene, $C^{12}H^{10}N^2O$, is also produced by fusing azobenzene-sulphonic acid, $C^{12}H^8N^2.SO^2H$, with potash (Griess, *Lieb. Ann.* cliv. 208), and by the action of diazobenzene nitrate on an aqueous solution of potassium phenate, whereupon it separates as a resin which soon becomes crystalline (Kekulé a. Hidegh, *Ber.* iii. 233). Treated with alcoholic ammonium sulphide, it is converted into a base, probably $C^{12}H^{12}N^2O$ (Griess). On heating it at 100° with phosphorus pentachloride, hydrochloric acid is evolved, and a crystalline body is formed, probably *hydroxy-*

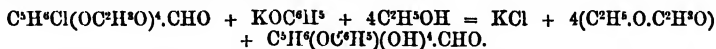
azoxybenzene, $O \begin{array}{c} \diagup N.C^6H^5 \\ \diagdown N.C^6H^4OH \end{array}$, which separates from alcohol in long orange-yellow needles (Kekulé a. Hidegh).

Phenol-didiazobenzene, $C^{18}H^{14}N^4O = C^6H^5(OH) \begin{array}{c} \diagup N.C^6H^5 \\ \diagdown N.C^6H^5 \end{array}$, is formed on mixing a solution of phenol-diazobenzene in potash with an aqueous solution of diazobenzene nitrate, and separates as a brown-rod precipitate easily purified by crystallisation from alcohol. Its formation is represented by the equation $C^{12}H^{10}N^2O + C^6H^4N^2 = C^{18}H^{14}N^4O$ (Griess, *Ber.* ix. 637).

An isomeric compound, perhaps $\begin{array}{c} N=N.C^6H^4.C^6H^4.OH \\ N=N.C^6H^5 \end{array}$, is formed by the action of potassium phenate on diazo-diamidobenzene. When treated with nascent hydrogen it yields aniline, paradiamidobenzene, and paramidophenol (Caro a. Schraube, *Chem. Centr.* 1878, 558).

Phenol-diazobenzo-diazotoluene, $C^{18}H^{16}N^4O$, is formed in like manner when an alkaline solution of phenoldiazobenzene is mixed in molecular proportion with diazotoluene nitrate (from paratoluidine). By recrystallisation from hot alcohol, with addition of animal charcoal, it is obtained in small brownish-yellow nodules melting at 110° . It agrees closely in its properties with phenol-didiazobenzene (Griess, *Ber. loc. cit.*)

Phenol-glucoside, $C^{12}H^{16}O^6 = C^6H^5(OC^6H^5)(OH)^4.CHO$ (A. Michael, *Compt. rend.* lxxxix. 355). This compound is formed, together with ethyl acetate, on mixing the alcoholic solutions of potassium phenate and acetochlorhydrate (p. 12), whereupon potassium chloride separates out, and on leaving the filtrate to evaporate, phenol-glucoside is deposited in long silky needles:

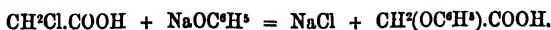


Phenol-glucoside melts at 171° – 172° , dissolves in water forming a dextrogyrate solution, and when boiled with aqueous potash or with dilute sulphuric or hydrochloric acid, is resolved into glucose and phenol: $C^{12}H^{16}O^6 + H^2O = C^6H^{12}O^6 + C^6H^5O$.

Orthoformyl-phenol-glucoside, $C^{13}H^{16}O^7 = C^6H^5(OC^6H^4.CHO)(OH)^4.CHO$, produced in like manner by the action of acetochlorhydrate on potassium salicylate, forms white needle-shaped crystals, which melt at 175° and decompose at a higher temperature.

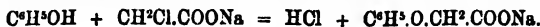
The action of acetochlorhydrate on sodium-saligenin appears to give rise to the glucoside of saliretin.

Phenolglycollic or Phenoxylacetic Acid, $C^6H^5O^3 = CH^2(OC^6H^5).COOH$. Heintz obtained acid this (ii. 918) by heating monochloracetic acid with sodium-phenol at 150° :



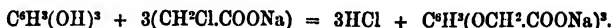
A more advantageous mode of preparation is to melt together equivalent quantities of

phenol and chloracetic acid on the water-bath, and add soda-ley (sp. gr. 1.3), slowly and with continual stirring, in quantity equal to about four times that of the phenol :



The reaction is soon completed, and the liquid on cooling solidifies to a crystalline mass of sodium phenol-glycolate which, when decomposed with hydrochloric acid, yields the free acid (Giacosa, *J. pr. Chem.* [2], xix. 396).

In like manner pyrogallol (1 mol.) reacts with sodium chloracetate (3 mol.) to form the sodium salt, $\text{C}^6\text{H}^3(\text{OCH}^2\text{COONa})^3$, which, when decomposed by dilute hydrochloric acid, yields pyrogallol-glycollic acid :



Pyrogallol-glycollic acid crystallises from aqueous solution in long colourless needles melting at 198°. The normal potassium salt is precipitated by alcohol from its aqueous solution in white needles, and on adding acetic acid to this solution a slightly soluble monopotassic salt, $\text{C}^6\text{H}^3\text{O}^3\text{K} + \text{H}^2\text{O}$, is precipitated (Giacosa).

Phenol-lactic or Phenoxypropionic Acid, $\text{C}^6\text{H}^4\text{O}^3 = \text{CH}^2\text{CH}(\text{OC}^6\text{H}^5).\text{COOH}$, formed by the action of sodium-phenate on α -chloropropionic acid, crystallises from hot water in shining needles, which melt at 112°–113°. On adding bromine-water to its hot aqueous solution, *bromophenol-lactic acid*, probably $\text{CH}^2\text{CH}(\text{OC}^6\text{H}^4\text{Br}).\text{COOH}$, is produced (Saarbach, *J. pr. Chem.* [2], xix. 175).

Phenol-phthalein. See PHTHALEINS.

Phenolphosphenylic Acid, $\text{C}^6\text{H}^5\text{PO}(\text{OH})\text{O.C}^6\text{H}^5$, is formed by the action of boiling water on the chloride, $\text{C}^6\text{H}^5(\text{PO})\text{ClO}$, produced, together with phenyl phosphenylate, by the action of phosphorus oxychloride on phenol. This acid forms long capillary needles melting at 57°, slightly soluble in water, easily in alcohol, ether, benzene, and alkalis. Its *ammonium salt* forms colourless needles; the *silver salt*, needles having a silky lustre (Michaelis a. Kammerer, *Ber.* viii. 48).

Phenol-sulphonic Acids, $\text{C}^6\text{H}^4\text{OH.SO}^3\text{H}$. The *meta*-acid, $[\text{OH} : \text{SO}^3\text{H} = 1 : 3]$, hitherto but little known, has lately been studied by Barth a. Senhofer (*Ber.* ix. 969), who prepare it as follows: Benzene-metadisulphonic acid dissolved in the smallest possible quantity of water, is heated at 170°–180° with two or three times its weight of potassium hydrate in a silver basin. The solution gradually becomes more and more concentrated until it acquires a thick pulpy consistence, at which stage the heating must be stopped. The product is then dissolved in water, neutralised with sulphuric acid, and evaporated, and the residue is exhausted with absolute alcohol, which takes up potassium phenolmetasulphonate, leaving potassium sulphate undissolved. The alcoholic solution, when evaporated, deposits crystals of the potassium salt, from which the free acid is obtained by adding to it the necessary quantity of sulphuric acid and a little water, evaporating to a syrup, agitating this with a mixture of alcohol and ether, filtering from potassium sulphate, and distilling with water. The acid thus obtained in aqueous solution is purified by converting it into lead-salt, decomposing the latter with hydrogen sulphide, and evaporating the liquid to a syrup, which gradually deposits the acid in delicate needles. The crystals dried in a vacuum contain 2 mols. of water: at 100°–112° they retain $\frac{1}{2}$ mol., which is expelled at 140°. The acid gives a violet coloration with ferric chloride.

The *potassium salt*, $\text{C}^6\text{H}^4(\text{HO})\text{SO}^3\text{K.H}^2\text{O}$, crystallises in a mass of small needles, which melt at 200°–210°, and effloresce in the air. A *basic potassium salt*, obtained by dissolving the normal salt and the necessary quantity of potash in alcohol, crystallises in silky needles. The *barium salt*, $(\text{C}^6\text{H}^4.\text{HO.SO}^3)^2\text{Ba}$, forms laminae very easily soluble in water. The *copper salt*, $(\text{C}^6\text{H}^4.\text{HO.SO}^3)^2\text{Cu} + 6\text{H}^2\text{O}$, crystallises in large bright-green rhombic tables, very freely soluble in water. The dried salt is extremely hygroscopic, taking up water from calcium chloride. The *lead salt*, $(\text{C}^6\text{H}^4.\text{HO.SO}^3)^2\text{Pb} + 3\text{H}^2\text{O}$, forms colourless quadratic tables. The *silver salt* crystallises in delicate needles, which dissolve easily in water. The *ammonium salt* crystallises from strong solutions in slender needles, and from dilute solutions in tables: it is freely soluble in water. The *sodium salt* crystallises with 1 mol. of water in large rhombic tables.

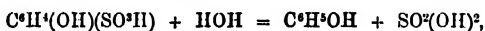
Potassium phenolmetasulphonate, heated to 250° with potash, exchanges the group SO^3H for HO , yielding resorcinol free from quinol or catechol. This behaviour of the *meta*-acid distinguishes it from the isomeric acids, neither of which yields resorcinol when similarly treated.

The following table exhibits the differences characteristic of some of the salts of the three phenolsulphonic acids :

Salt	Ortho-acid	Meta-acid	Para-acid
K	Melts at 240°. Crystallises in long flat needles, with 2 mols. water.	Melts at 200°. Crystallises in masses of confused microscopic needles with 1 mol. water.	Does not melt at 260°. Crystallises in anhydrous hexagonal tables.
Ba	Indistinctly crystalline masses with 2 mols. water. Very soluble in water.	Small laminae, composed of microscopic needles, containing $\frac{1}{2}$ mol. water.	Long silky matted needles, containing 3 mols. water.
Pb	Indistinct tables, with 1 mol. water. Dissolves with great difficulty in water.	Crystallises in large rhombic tables, containing 3 mols. water.	Long needles grouped in nodules. Contains 2 mols. water.
Cu	Pale-blue prisms.	Large thin bright green rhombic tables, containing 6 mols. water.	Thick blue plates, resembling cupric sulphate. Contains 10 mols. water.
Na	Indistinctly crystalline masses, containing $1\frac{1}{2}$ mol. water.	Flat needles, or large rhombic tables, with 1 mol. water.	Prismatic crystals, containing 2 mols. water.

Phenolparasulphonic acid oxidised with manganese dioxide and sulphuric acid yields a large quantity of quinone; the meta-acid yields none (Schrader, *Ber.* viii. 759).

Conversion of Phenol-orthosulphonic acid into the Para-modification.—The ortho-acid, in presence of water, is resolved at comparatively low temperatures into phenol and sulphuric acid :



the sulphuric acid then acting further on the phenol, and producing a mixture of the ortho- and para-acids, provided the temperature of decomposition of the ortho-acid has not been exceeded.

The ortho-acid is not the sole product of the action of sulphuric acid on phenol at low temperatures, considerable quantities of the para-acid being always formed, even at 0°.

When the potassium salt of phenol-orthosulphonic acid is heated with excess of sulphuric acid in sealed tubes, there separates after a time a reddish-brown oily layer of phenol, which, when the tube is more strongly heated, disappears either partially or entirely, according to the strength of the solution, and forms a dark-red liquid, doubtless containing free sulphuric and phenolparasulphonic acids. When a concentrated aqueous solution of the same salt is heated with a quantity of sulphuric acid insufficient for complete decomposition, the separation of phenol takes place much more slowly. It seems probable that the conversion of ortho- into para-acid would not take place in the absence of sulphuric acid (Post, *Ber.* viii. 1547).

The crystalline form of potassium parasulphonate has been examined by C. Bode-wig. The crystals are orthorhombic, having the axial ratio $a : b : c = 0.8790 : 1 : 1.0017$. Observed faces $P, \infty P, \infty \bar{P}$. The crystals are tabular according to $\infty \bar{P}$, and have no distinct cleavage. Angle, $\infty P : \infty P = 82^\circ 12'$; $P : \infty P = 33^\circ 8'$. The plane of the optic axes is OP ; the axis b is the first median line. Double refraction positive.

Dihydroxybenzene-sulphonic acid, $\text{C}^6\text{H}^3\text{SO}^2\text{H.H.OH.OH.H}^2$.—The potassium salt of this acid is formed by the action of melting potash on that of the corresponding phenol-disulphonic acid, $\text{C}^6\text{H}^2\text{SO}^2\text{H.H.SO}^2\text{H.OH.H}^2$ (vi. 926); and on decomposing it with hydrochloric acid, and leaving the solution to evaporate, dihydroxybenzene-sulphonic acid is obtained in needle-shaped crystals. The aqueous solutions of this acid have a strong acid reaction, and give with ferric chloride an intense green coloration, which becomes successively blue, violet, and red on the addition of sodium carbonate. These colour-reactions are similar to those obtained with protocatechuic acid (p. 289), to which, in fact, the sulphonic is analogous in constitution, containing SO^2H in place of CO^2H . Lead acetate gives no precipitate with the aqueous solutions of the acid or its salts, but basic lead acetate gives a white precipitate.

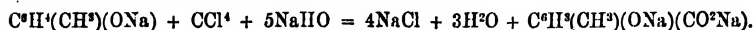
The potassium salt, $\text{C}^6\text{H}^3(\text{OH})^2.\text{SO}^2\text{K}$, is easily soluble in water, and sparingly in

absolute alcohol. The *sodium salt*, $C^6H^3(OH)^2.SO^3Na + H^2O$, crystallises in colourless prisms. The *barium salt*, $[C^6H^3(OH)^2.SO^3]^2Ba$, is easily soluble in water, and crystallises from alcohol in needles united in concentric masses. The acid fused with potash yields catechol or orthodihydroxybenzene.

Sulphoxybenzene-phenols. This name was given by Griess (*Ber.* xi. 2191) to a series of compounds obtained by the action of alkaline solutions of phenols and their derivatives on the diazobenzenesulphonic acids and other diazo-compounds. See SULPHONIC ACIDS.

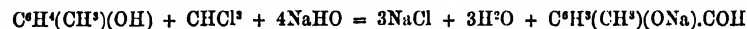
PHENOL: HOMOLOGUES OF. I. Cresols. 1. The isomeric cresols, $C^6H^4(CH^3)(OH)$, and several of their derivatives have already been described in vol. vii. pp. 931-934, and this volume, pp. 581-584.

Conversion of Cresols into Hydroxytoluic Acids and Aldehydes.—The three isomeric cresols, treated in strongly alkaline solution with carbon tetrachloride, are converted into hydroxytoluic acids, $C^6H^4(OH)(CH^3).CO^2H$, viz. homosalicylic and homoparahydroxybenzoic acids, according to the equation:



By this reaction *ortho*-cresol gives orthohomosalicylic and orthohomoparahydroxybenzoic acids, $[OH : CH^3 : CO^2H = 1 : 2 : 6 \text{ and } 1 : 2 : 4 \text{ respectively}]$; *meta*-cresol gives metahomosalicylic and metahomoparahydroxybenzoic acids, $[OH : CH^3 : CO^2H = 1 : 3 : 6 \text{ and } 1 : 3 : 4]$, together with another acid, probably parahomohydroxyisophthalic acid, and *para*-cresol gives only parahomosalicylic acid, $[OH : CH^3 : CO^2H = 1 : 4 : 6]$ (C. Schall, *Ber.* xii. 816). See TOLUIC ACIDS (HYDROXY-).

The corresponding hydroxytoluic aldehydes, $C^6H^4(OH)(CH^3).COH$, are obtained in like manner by treating the three cresols in alkaline solution with chloroform:



(Tiemann a. Schotten, *Ber.* xi. 767). See TOLUIC ALDEHYDES.

Tetrabromoparacresol, $C^6H^3Br^4O$.—When bromine-water is added to an aqueous solution of pure paracresol until a permanent colour is obtained, a cloudiness is first produced, and in a short time crystalline plates of tetrabromoparacresol are deposited, which, after rapid filtering and drying over sulphuric acid, melt at 109° . This substance, on keeping, gradually undergoes decomposition. The yield of the bromophenol is always less than the calculated quantity.

If the precipitate be left over night in contact with the bromine-water, it is partly converted, with evolution of carbon dioxide, into tribromophenol (m. p. 91°), whereby the proportion of bromine in it is lowered by about 2 per cent.; this change taking place more rapidly and completely when the temperature is raised to 30° - 40° (Bauermann a. Brieger, *Ber.* xii. 804).

Nitrocresols.—See p. 583.

Cresolsulphonic acids.—vii. 932; viii. 583.

II. Xylenols, $C^6H^4O = C^6H^3(OH)(CH^3)^2$ (O. Jacobsen, *Ber.* xi. 23). Four of these compounds are known, and are distinguished by the prefixes, *ortho*-, *meta*-, and *para*-, according to the xylenes from which they are derived, viz.:

	CH ^a	CH ^b	OH
Ortho-xylenol	1	2	4
α -Meta-xylenol	1	3	4
β -Meta-xylenol	1	3	2
Para-xylenol	1	4	2

They are prepared by fusing the potassium salts of the corresponding xylenesulphonic acids, $C^6H^3(CH^3)^2SO^3K$, with four times their weight of potassium hydroxide; acidulating the melt with hydrochloric acid; shaking it up with ether; treating the ethereal solution with sodium carbonate, to remove hydroxytoluic acids, which are always formed at the same time in small quantity; drying the product with calcium chloride; removing the ether by evaporation; and distilling the xylenol which remains behind. The yield is very satisfactory, sometimes amounting to more than three-fourths of the calculated quantity.

(1). **Orthoxylenol** crystallises from water in very long needles, from alcohol of 8 to 10 per cent. in large rhombic octohedrons, melts at 61° , and boils at 225° (bar.

757 mm.) Its *sodium salt*, C^8H^7ONa , is but slightly soluble in cold strong soda-ley, and crystallises from the hot solution in very large flattened needles having a silky lustre. Tribrom-*o*-xylenol, $C^8H^4Br^3OH$, crystallises from hot alcohol in woolly masses of thin snow-white needles melting at 169° .

Orthoxylenol forms only one sulphonic acid, the *sodium salt* of which, $C^8H^6(OH)SO^3Na$, crystallises in very fine long flat anhydrous prisms, or on quicker separation, in small laminae, mostly united in large hemispherical groups. The *barium salt*, $(C^8H^6OHSO^3)^2Ba$, is somewhat sparingly soluble in cold water, and separates on cooling from the hot solution, or on slow evaporation, in hard nodular crusts, or separate hemispherical nodules consisting of microscopic rhombic laminae. The *copper salt* and the very soluble *zinc salt* crystallise well. The salts give a violet reaction with *ferrie chloride*.

(2). ***α*-Metaxylenol**, [1 : 3 : 4]. This modification, which forms the principal part of the xyleneol described by Wurtz, Wroblevsky (vi. 1129), and Lako (*Liebig's Annalen*, clxxxii. 30) differs from all the other xyleneols in being liquid at ordinary temperatures. It is colourless, strongly refractive, has a phenolic odour, does not solidify at -20° , but merely becomes viscid; boils constantly at 211.5° (bar. 766 mm.; mercury-column wholly in the vapour). Sp. gr. 1.0632 at 0° . It mixes in all proportions with alcohol and ether, but dissolves very sparingly in water. The aqueous solution is coloured blue by *ferrie chloride*; the alcoholic solution green. The *sodium salt*, C^8H^7ONa , differs from its isomerides in being easily soluble in strong soda-ley.

Bromo-α-metaxylenol, $C^8H^6Br(OH)$, obtained by the action of bromine on the solution of the xyleneol in acetic acid, is a colourless oily liquid, decomposing when distilled. The *dibromo-derivative*, $C^8H^4Br^2.OH$, separates on dropping water into its alcoholic solution in long slender colourless needles melting at 73° . The *tribromo-derivative*, $C^8H^2Br^3.OH$, crystallises from hot alcohol in long perfectly colourless needles, melting at 179° .

Sulphonic acids.—On agitating *α*-metaxylenol with an equal volume of ordinary sulphuric acid, two sulphonic acids are formed, and crystallise after a while in stellate groups of needles. On adding a small quantity of water, one of these acids separates in greatest abundance, forming white rhombic laminae. The two acids may, however, be more completely separated in the form of barium salts, $[C^8H^6(OH)SO^3]^2Ba$, that of the acid which separates in rhombic laminae crystallising out first from the aqueous solution in anhydrous rectangular laminae or thicker rectangular tablets, which often look like irregularly formed cubes. This salt dissolves somewhat sparingly in cold, much more readily in hot water. The *potassium salt* of the same acid, which is not very soluble in cold water, crystallises in dendritic groups of colourless anhydrous laminae. The *sodium salt* forms large anhydrous tablets. The *barium salt* of the second sulphonic acid is obtained in microscopic needles by evaporating the mother-liquor of the first; the *sodium salt*, $C^8H^6OH.SO^3Na + 4H^2O$, forms large laminae.

Acetyl-α-metaxylenol, $C^8H^6O(C^2H^3O)$, is a colourless liquid having a faint odour like that of bergamot-oil, not miscible with water, boiling at 226° (bar. 760 mm.)

Methyl-α-metaxylenol, $C^8H^6O(CH^3)$, is also a colourless liquid, which does not solidify at low temperatures, boils at 192° , and has a very faint odour resembling that of the pure hydrocarbons of the benzene series. Treated at low temperatures with excess of bromine, it yields a tribromo-derivative, $C^8H^6Br^3.OCH^3$, which dissolves rather sparingly in cold, more freely in hot alcohol, and crystallises in large flat colourless needles melting at 120° .

(3). ***β*-Metaxylenol**, $[CH^3 : OH : CH^3 = 1 : 2 : 3]$, crystallises from water in silky laminae or long flat needles, melts at 74.5° , and boils at 211° – 212° . With bromine it forms a *tribromo-derivative*, which crystallises from alcohol in long light yellow needles melting at 175° . With sulphuric acid it forms two *sulphonic acids*, only one of which yields a distinctly crystallised barium salt.

(4). ***Paraxylenol***, $[CH^3 : OH : CH^3 = 1 : 2 : 4]$, crystallises from dilute alcohol in large flat needles, melting at 74.5° , and sublimes a little above its melting point in small woolly needles. It boils at 211.5° (bar. 762 mm.), and, like its isomerides, volatilises readily with vapour of water. Its aqueous solution is not coloured by *ferrie chloride*. The *sodium-derivative*, C^8H^7ONa , is very slightly soluble in cold concentrated soda-ley, and separates on cooling from the hot solution in large crystalline laminae.

Monobromo-p-xyleneol, $C^8H^6Br.OH$, obtained by bromination in acetic acid solution, precipitation with water, and crystallisation from dilute alcohol, forms a loose colourless mass of long flexible needles melting at 87° . *Tribromo-p-xyleneol*, $C^8H^4Br^3.OH$,

formed by adding excess of bromine to cooled paraxyleneol, crystallises from hot alcohol in long needles of deep golden-yellow colour, and melts at 175° .

Paraxyleneol, dissolved in moderately warm sulphuric acid, yields only one sulphonic acid, which separates on addition of water in hydrated laminae. Its *barium salt*, $(C^6H^4OHSO^3)^2Ba$, crystallises in stellate or larger nodular groups of microscopic anhydrous needles which begin to decompose at 115° . The *sodium salt*, $C^6H^4OH.SO^3Na + 5H^2O$, crystallises in large very fine rhombic tablets, having an acute angle of 86.5° , and efflorescing in dry air at ordinary temperatures.

Acetyl-p-xyleneol, $C^6H^3.O.C^2H^3O$, is a colourless liquid, not solidifying at -20° , having a faint odour somewhat like that of bergamot-oil, a sp. gr. of 1.0264 at 15° , and boiling at 237° (bar. 768 mm.)

Methyl-p-xyleneol, $C^6H^3.O.CH^3$, is a colourless non-solidifying liquid smelling like the pure benzene-hydrocarbons, and boiling at 194° (bar. 772 mm.)

The salts of the above-described xyleneolsulphonic acids give a deep violet coloration with ferric chloride.

The xyleneols are converted by prolonged fusion with potassium hydroxide into hydroxytoluic acid, $C^6H^3(CH^3)(OH).CO^2H$, and hydroxyphthalic acid, $C^6H^3(OH)(CO^2H)^2$.

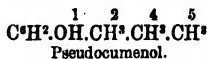
III. Nine-carbon-phenols, $C^6H^{10}O = C^6H^4OH(C^3H^7)$. 1. **Normal Propylphenols**, $C^6H^4(OH).CH^2.CH^2.CH^3$ (P. Spica, *Gazz. chim. ital.* 1878, 406). Two of these compounds, $[OH : C^3H^7 = 1 : 2 \text{ and } 1 : 4]$, are obtained by the action of melting potash on the corresponding propylbenzenesulphonic acids, $C^6H^4(C^3H^7)SO^3H$, which are produced by treating normal propylbenzene with sulphuric acid, and separated by means of their barium salts. The *para*-compound, also called *α-propylphenol*, is a colourless liquid boiling at 230.6° – 232.6° (corr.), and having a density of 1.0091 at 0° and 0.9324 at 99.8° . The *acetyl-derivative*, $C^6H^4(C^3H^7)OC^2H^3O$, is a colourless liquid having a density of 1.02904 at 0° and 0.94229 at 100° , and boiling between 242.7° and 244° (corr.) The *methyl ether*, $C^6H^4(C^3H^7)OCH^3$, is a colourless liquid having a pleasant odour of anise, boiling between 214° and 215.5° , and having a density of 0.96364 at 0° and 0.91251 at 99.6° . By oxidation with potassium dichromate and sulphuric acid, it is converted into anisic acid. Para-propylphenol, treated with carbon dioxide and sodium, is converted into the sodium salt of a *p*-propylphenolcarboxylic acid represented by the formula $C^6.C^3H^7.H.CO^2OH.OH.H^2$. This acid melts at 98° , and its aqueous solution produces a violet colour with ferric chloride. Its *barium salt* crystallises with 3 mol., the *lead salt* with 2 mol. H^2O . The *silver salt* has the composition $C^{10}H^{11}O^3Ag$.

Ortho-, or *β*-Propylphenol, is a colourless liquid which distils at 224.6° – 226.6° (corr.), and has a density of 1.0156 at 0° , and 0.93702 at 99.8° ; its aqueous solution is coloured violet by ferric chloride. The *methyl ether* boils between 207° and 209° (corr.), and has a density of 0.96944 at 0° , and 0.916772 at 99.88° . *o*-Propylphenolcarboxylic acid, probably $C^6.C^3H^7.OH.CO^2OH.H^2$, forms barium and lead salts which crystallise with $2\frac{1}{2}H^2O$. The *silver salt*, $C^{10}H^{11}O^3Ag$, is a white precipitate.

2. **Isopropyl-phenol, Cumophenol, or Cumenol**, $C^6H^4\begin{smallmatrix} CH(CH^3)^2 \\ OH \end{smallmatrix}$, produced

by fusing potassium cumenesulphonate with potassium hydroxide, melts at 61° and boils at 228.2° – 229.2° (corr.) Its *methyl ether*, $C^6H^4(C^3H^7)(OCH^3)$, is a colourless liquid smelling like oil of anise, having a density of 0.962 at 0° , and boiling at 212° – 213° (bar. 758.04 mm.) When oxidised with potassium dichromate and sulphuric acid, it yields a small quantity of anisic acid. The *ethyl ether* has a density of 1.026, and boils at 244° – 245° (bar. 756.27 mm.) (Paterno a. Spica, *Gazz. chim. ital.* 1876, 535; *Ber.* ix. 455).

3. **Trimethyl-phenols**, $C^6H^3(OH)(CH^3)^3$. Two of these compounds are known, viz.:



Mesitol, which Biedermann a. Ledoux obtained by the decomposition of diazo-mesitylene nitrate, and by the action of melting potash on potassium mesitylenesulphonate (p. 1282), has been further studied by Jacobsen (*Liedig's Annalen*, excv. 265), who prepares it by the last-mentioned reaction. It melts at 68° , boils at 219.5° (bar. 763 mm.), and dissolves in a strong sulphuric acid, yielding a sulphonic acid, which forms an easily soluble barium salt crystallisable in small needles. The sodium salt is also easily soluble in water and crystallises in flat prisms. Ferric chloride colours the aqueous solutions of these salts deep blue.

Monobromomesitol prepared by acting on mesitol dissolved in glacial acetic acid, with bromine in the cold, crystallises from hot dilute alcohol in white, long, flexible, silky needles (m. p. 80°), and is identical with the compound described by Biedermann and Ledoux.

Dibromomesitol is formed by acting on the monobromo-derivative with bromine, or by dissolving mesitol in an excess of well-cooled bromine. It is soluble in hot water, more easily in a hot aqueous solution of an alkaline carbonate, from which it separates on cooling, and is obtained by crystallisation from alcohol, in large, brittle, colourless prisms, melting at 150° . It cannot be volatilised without decomposition. If the bromine used in the preparation of this body contains moisture, a second compound is formed, which is the only product of the action when bromine acts on mesitol and water. This compound is more soluble in alcohol than dibromomesitol, crystallises in large acute golden-yellow rhombic plates, melting at 174° (corr. 176°), and subliming in shining golden-yellow leaflets. It is insoluble in water and in alkaline carbonates. It is decomposed by potash, forming a dark brown solution, from which, after acidifying with hydrochloric acid, ether extracts a new compound, in the form of a semi-liquid mass, which becomes crystalline after some time; it is soluble in alcohol, yielding a dark brown solution, which is decolorised by sodium-amalgam, but becomes brown again on exposure to air. This compound is identical with Fittig a. Hoogewerff's dibromoxyleneol (vi. 1129); its properties are, however, those of a quinone, and analysis shows it to have the composition of *dibromoxylenequinone*, $C^8H^6Br^2O^2$. Mesitol fused with potash is converted into hydroxymesitylenic acid, $C^8H^{10}O^3$ (see ADDENDA).

Pseudocumenol, $C^8H^2OH(CH^3)^3$ (A. Reuter, *Ber.* xi. 29).—This compound is formed by fusing pseudocumenesulphonic acid (p. 1285) with potassium hydroxide. It is nearly insoluble in cold water, very easily soluble in alcohol and ether, volatilises very easily with vapour of water, and solidifies for the most part in the condensing tube to a white crystalline mass having a phenolic odour. When distilled by itself, it yields a loosely coherent crystalline mass composed of thin flexible needles. Its solutions are not coloured by ferric chloride.

Bromopseudocumenol, C^8H^2BrOH , formed by careful bromination of pseudocumenol dissolved in acetic acid, crystallises from dilute alcohol in long colourless needles, melts at 32° , and boils with partial decomposition at about 250° . *Dibromopseudocumenol*, $C^8H^2Br^2OH$, formed by the action of excess of bromine on cooled pseudocumenol, crystallises from hot alcohol in large hard colourless needles melting at 149° – 150° .

Pseudocumensulphonic acid, $C^8H^{10}(OH)(SO^3H)$, separates after some time from a solution of pseudocumenol in strong sulphuric acid, in small shining crystals having the form of cupric sulphate. On carefully mixing it with water, especially in the form of lumps of ice, a crystalline pulp is formed consisting of the hydrated acid. The sulphonic acid, when free from sulphuric acid, is very unstable, and decomposes in moist air, even at ordinary temperatures, into sulphuric acid and pseudocumenol. Its salts decompose at 100° . The *potassium salt* and the *zinc salt* crystallise in rather large elongated laminae; the *copper salt* in indistinctly crystalline nodules; the comparatively sparingly soluble *barium salt* in nodular groups of shining laminae.

Constitution of Pseudocumenol and its Derivatives.—Pseudocumenol, subjected to prolonged fusion with potassium hydroxide, is converted into hydroxy-xylic acid, $C^8H^2(CH^3)^3OH.CO^2OH$, which may be extracted with caustic soda from the solution obtained by agitating the acidulated melt with ether, and purified by distillation with steam. It is but slightly soluble in boiling water, nearly insoluble in cold water, and crystallises from the hot aqueous solution in feathery groups of needles, or by slower cooling in small compact prisms, apparently orthorhombic. It is readily soluble in alcohol and ether, melts at 195° , but sublimes readily between 160° and 170° in feathery groups of microscopic prisms. With ferric chloride it produces a deep violet colour. The *barium salt* forms small compact hydrated crystals; the *calcium salt* dries up in a vacuum to an amorphous mass. Since now this calcium salt, when distilled with excess of lime yields the liquid 1 : 3 : 4 *m*-xyleneol (p. 1541) and moreover potassium pseudocumenesulphonate when fused with sodium formate yields the same cumylic or durylic acid (vi. 828) that is produced by oxidation of durene (tetramethylbenzene), it follows that the compound under consideration must be represented by the following constitutional formulæ

	1	2	3	4	5	6
Pseudocumene	—	CH ³	—	CH ³	CH ³	—
Liquid <i>m</i> -xylene	OH	CH ³	—	CH ³	—	—
Hydroxy-xylic acid	OH	CH ³	—	CH ³	CO ² H	—
Pseudocumenol	OH	CH ³	—	CH ³	CH ³	—
Pseudocumene-sulphonic acid	SO ³ H	CH ³	—	CH ³	CH ³	—
Cumylic or Durylic acid	CO ² H	CH ³	—	CH ³	CH ³	—
Durene	CH ³	CH ³	—	CH ³	CH ³	—

IV. **Cymphenols** or **Cymenols**, $C^{10}H^{11}O = C^6H^3(CH^3)(C^4H^7)OH$. Two of these phenols are known, viz:

	OH	CH ³	C ⁴ H ⁷
Thymol	1	3	6
Carvacrol	1	2	5

Thymol, obtained from the volatile oils of thyme, horse-mint, *Ptychotis Ajowan*, and *Monarda punctata*, melts at 44° and boils at 230°; *carvacrol*, obtained by fusing cymene-sulphonic acid with potash, by heating camphor with iodine, and from the isomeric compound carvol, contained in oil of caraway, by heating with phosphoric acid, is an oil not solidifying at -25°, boiling at 233°-235° (i. 809; v. 793-4).

The following derivatives of these isomeric phenols have been examined by Paternò (*Gazz. chim. ital.* 1875, 13).

The *acetyl*- and *methyl*-derivatives are identical in boiling point and specific gravity, as may be seen from the following table:

	From thymol	From carvacrol
Acetate $C^{10}H^{11}.O.C^2H^3O$ { B. p. (corr.) 244.7°		245.8°
Sp. gr. at 0° = 1.009		1.010
" " 100° = 0.924		—
Methylate $C^{10}H^{11}.O.CH^3$ { B. p. (corr.) 216.7°		216.8°
Sp. gr. at 0° = 0.954		0.954
" " 100° = 0.869		0.870

The *ethylene*-derivatives, $C^{10}H^{13}O \left\{ \begin{matrix} C^{10}H^{13}O \\ C^{10}H^{13}O \end{matrix} \right\} C^2H^4$, however, are different. The product obtained by adding ethylene bromide to an alcoholic solution of thymol mixed with alcoholic potash, boiling the whole for some hours in an apparatus with reversed condenser, and dissolving out the resulting potassium bromide with water, is solid at ordinary temperatures, and crystallises from ether in beautiful laminae melting at 99°, whereas the corresponding derivative of cymene-thymol does not appear to be crystallisable.

Barth (*Ber.* xi. 567), by fusing thymol with potassium hydroxide, has obtained four acids, viz. (1) hydroxybenzoic acid; (2) hydroxyterephthalic acid; (3) thymol-hydroxycinnamic acid, $C^{10}H^{11}O^2$, which forms needle-shaped crystals melting at 143°; (4) a dibasic acid (which Barth proposes to call *thymolic acid*), easily soluble in water, the aqueous solution precipitating lead salts and producing a deep red coloration with ferric chloride.

Dinitrothymol, $C^{10}H^{11}(NO_2)^2OH$. — The ethylic ether of this compound, $C^{10}H^{11}(NO_2)^2OC^2H^5$, obtained by heating the sodium salt in sealed tubes at 140°-150° with ethyl iodide and alcohol, crystallises in colourless plates, melts at 52°-53°, dissolves easily in alcohol and ether, and decomposes when distilled. By reduction with tin and hydrochloric acid it yields a lead salt which is converted by distillation with aqueous ferric chloride into hydroxythymoquinone and dihydroxythymoquinone.

Dinitrothymol, heated with phosphorus pentachloride, is converted into chloro dinitrocymene, $C^{10}H^{11}Cl(NO_2)^2$, which melts at 100°-101°, is moderately soluble in alcohol and ether, less freely in carbon sulphide and chloroform. By reduction with tin and hydrochloric acid, chlorodinitrocymene is converted into an amido-compound which, when oxidised with chromic acid mixture, yields dihydroxythymoquinone, $C^{10}H^{10}(OH)^2O^2$ (vii. 1156), and chlorhydroxythymoquinone, $C^{10}H^{10}(OH)ClO^2$ (Ladenburg & Engelbrecht, *Ber.* x. 1218). See THYMOQUINONES.

Nitrosothymol, $C^{10}H^{11}(NO)O$, is prepared by mixing a solution of thymol in potash with a solution of potassium nitrite, diluting the mixture with a large quantity of water, and adding dilute sulphuric acid, whereupon the whole liquid is speedily converted into a magma of crystals, which are to be thrown upon a cloth filter and washed, then dried and crystallised from benzene. The product, after repeated crystallisation from chloroform, forms small needles melting at 155°-156°. It is nearly

insoluble in water, but dissolves easily in alcohol, ether, and chloroform. It dissolves in alkalis with red coloration, also in strong sulphuric acid, from which it is deposited on addition of water.

The alkali-salts, obtained by dissolving nitrosothymol in potash or soda, form long yellow needles. Their solutions are decomposed by carbonic acid. The salts of the heavy metals are coloured amorphous precipitates. The *benzoyl-ether*, $C^{10}H^{11}NO^2$, formed by heating the potassium-salt with benzoyl chloride, crystallises from absolute alcohol in fine yellow needles, melting at 110° .

Potassium ferricyanide in alkaline solution oxidises nitrosothymol to nitrothymol, which crystallises in concentric groups of needles melting at 137° . Strong nitric acid converts nitrosothymol into dinitrothymol. Tin and hydrochloric acid reduce it, forming amidothymol hydrochloride, $(C^{10}H^{13}O.NH^2.HCl)$, a white crystalline substance decomposing at 210° – 216° . Free amidothymol is very unstable. The action of nitrous acid upon nitrosothymol in ethereal solution results in the formation of a very easily decomposable diazo-derivative, the sulphate of which, $(C^{10}H^{11}N^2O.HSO^4)$, forms white crystals decomposing at 120° (R. Schiff, *Ber.* viii. 1500).

Nitrosocarvacrol, prepared in like manner, crystallises from benzene in lemon-yellow prisms melting at 153° , insoluble in water, soluble in alcohol, ether, benzene, and chloroform. By reduction with tin and hydrochloric acid, it is converted into amidocarvacrol, which crystallises in slender needles, having a silvery lustre and melting at 134° . By oxidation in alkaline solution with potassium ferricyanide, it is converted into nitrocarvacrol, which crystallises in pale yellow needles melting at 77° – 78° , slightly soluble in water, easily in alcohol and ether (Paternò a. Canzoneri, *Gazz. chim. ital.* 1878, 501).

Cymenol-sulphonic acids, $C^{10}H^{14}SO^2 = C^{10}H^{13}SO^2H$ (Paternò, *Gazz. chim. ital.* 1875, 13).—Engelhardt a. Latschinoff have shown that the chief product of the action of sulphuric acid on *thymol*, under ordinary circumstances, is a sulphonic acid (distinguished as α), which forms lead and barium salts containing $2H^2O$, and a potassium salt containing $2\frac{1}{2}H^2O$.

Carvacrol, heated for some hours in the water-bath with rather more than its own weight of ordinary sulphuric acid, dissolves almost completely, and on adding water and neutralising with barium carbonate, a mixture of two salts is obtained, one of which crystallises in anhydrous laminae yielding 28.44 per cent. baryta, while the other crystallises in needles containing $5H^2O$, or 15.12 per cent., and 23.02 per cent. BaO. The *lead-salt*, $(C^{10}H^{12}O.H.SO^2)^2Pb + 5H^2O$, crystallises in small shining needles very soluble in water. The *potassium salt* crystallises in shining needles containing a considerable quantity of water of crystallisation. On heating a solution of this potassium salt with dilute nitric acid, a heavy oil separates, which on cooling solidifies to orange-yellow crystals, soluble in ether and benzene, and slightly soluble in water. This substance melts at about 119° , and appears to be a nitrocymphenol.

Methyl-cymenolsulphonic acids, $C^{10}H^{12}(OCH^3)(SO^2H)$.—1. From Thymol. From the experiments of Engelhardt a. Latschinoff (*loc. cit.*), it appears probable that the action of sulphuric acid on the methylic ether of thymol gives rise to the formation of two isomeric sulphonic acids, one of which yields a crystallisable barium salt containing 3 mol. water, while the other yields an amorphous barium salt. Paternò's experiments confirm these results, and show that the products are the same whether the action takes place slowly at ordinary temperatures or quickly at the boiling heat. When 1 pt. of methyl-thymol is heated for several hours with $1\frac{1}{2}$ pt. sulphuric acid of $63^\circ B.$, and water is then added, an oily substance separates which crystallises on cooling; and the aqueous solution neutralised with barium carbonate deposits a well-crystallised barium salt, an additional quantity of which may be obtained from the mother-liquor, while the uncrystallisable salt mentioned by Engelhardt a. Latschinoff still remains dissolved.

The crystalline *barium salt*, $(C^{10}H^{12}.OCH^3.SO^2)^2Ba + 3H^2O$, forms large hexagonal plates having a vitreous lustre but becoming opaque after some time; it is nearly insoluble in cold, somewhat more soluble in hot water; gives off the whole of its crystallisation-water at 110° , and decomposes at a somewhat higher temperature. The *lead salt*, $(C^{10}H^{12}.OCH^3.SO^2)^2Pb + xH^2O$, forms very light, slender, shining needles, which do not give off all their water at 100° , and decompose at higher temperatures. The *potassium salt*, $C^{10}H^{12}.OCH^3.SO^2K$, crystallises from aqueous solution in large splendid anhydrous plates.

The oily substance already mentioned as produced by the action of sulphuric acid on methyl-thymol, and afterwards crystallising, may be purified by pressure between bibulous paper, and recrystallisation from ether or from benzene. It then forms small needles, melting at 150° – 151° , very soluble in benzene, slightly soluble in ether.

It is in all probability a compound analogous to sulphobenzide, and represented by the formula :



It gave by analysis 8.05 per cent. of sulphur, the formula requiring 8.87.

2. From Carvacrol.—A mixture of carvacrol with twice its weight of ordinary sulphuric acid, left to itself for a few hours, solidifies to a crystalline mass, soluble for the most part in water; and on neutralising the solution with barium carbonate, a barium salt is formed, which crystallises only from very strong solutions, forming a white mass, separable by washing on a filter with cold water into two salts, one of which (α) remains on the filter, and may be purified by recrystallisation from hot water, while the other (β) may be obtained by evaporating the wash-water. The α -salt, $(\text{C}^{10}\text{H}^{12}.\text{OCH}^3.\text{SO}^3)^2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, crystallises on cooling from its hot aqueous solution in small hard heavy prisms, having a vitreous lustre. The β -salt, $(\text{C}^{10}\text{H}^{12}.\text{OCH}^3.\text{SO}^3)^2\text{Ba} + 5\text{H}_2\text{O}$, is very soluble in water, and crystallises in very light and very white needles.

PHENOXYLIC ACID, $\text{C}^6\text{H}^5\text{O}^2 = \text{C}^6\text{H}^5.\text{CO}.\text{CO}.\text{OH}$. See PHENYL-GLYOXALIC ACID.

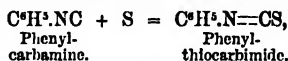
PHENYL (DI-) and its derivatives. See DIPHENYL (pp. 658–686).

PHENYL CARBAMATE, or **PHENYL-URETHANE**, $\text{NH}^2.\text{CO}.\text{OC}^6\text{H}^5$, See CARBAMATES (p. 384).

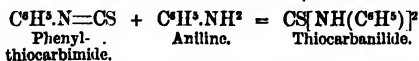
PHENYL CYANATE and **CYANURATE** are formed, together with benzoic acid and benzanilide, by the distillation of dibenzhydroxamic acid; the cyanate, also, together with anisanilide, from benzanishydroxamic acid (pp. 1080, 1081); methoxyl-phenyl cyanate, in like manner, together with benzoyl-anisidine and carbon dioxide, from anisbenzhydroxamic acid (Pieschel, *Liebigs Annalen*, clxxv. 305).

PHENYL CYANIDE, or **BENZONITRIL**, $\text{C}^6\text{H}^5-\text{C}\equiv\text{N}$, and **PHENYL ISO-CYANIDE** or **PHENYL CARBAMINE**, $\text{C}^6\text{H}^5-\text{N}\equiv\text{C}$. Phenyl-carbamine is produced by desulphuration of phenyl-thiocarbimide, $\text{CSN}(\text{C}^6\text{H}^5)$, with finely divided copper (precipitated from a strong solution of the sulphate with excess of zinc; Gladstone's copper-zinc couple), and subsequently changes into normal phenyl cyanide or benzonitril. This transformation also takes place when phenyl-carbamine, freed as far as possible from aniline by distillation, is heated for two or three hours at 200° – 220° in sealed tubes, or when phenyl-carbamide containing aniline is heated in an open vessel with reflux condenser. The nearly colourless oil which passes over on heating the product of this reaction with steam may be freed from aniline by dilute sulphuric acid, and, when again distilled, yields pure benzonitril boiling at 191° (Weith, *Ber.* vi. 210).

Phenyl-carbamine may be converted into phenyl-thiocarbimide and subsequently into diphenyl-thiocarbamide or thiocarbamilide, by acting upon it while in the nascent state with sulphur, that is to say by gently heating a mixture of aniline, chloroform, and alcoholic potash with sulphur for two or three hours. On pouring the product into water, scarcely any odour of phenyl-carbamine becomes perceptible, and a heavy oily liquid separates, which, when freed from aniline by dilute hydrochloric acid and from chloroform by heating, solidifies to a mass yielding on crystallisation from hot alcohol, laminae of thiocarbamilide resulting from the combination of the phenyl-thiocarbimide formed in the first instance with aniline:



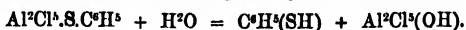
and



Phenyl-carbamine free from aniline is also converted into phenylthiocarbimide by direct addition of sulphur, the thiocarbimide being obtained in oily drops on distilling the product with steam. Benzonitril and sulphur do not react on one another in any way whatever (Weith, *loc. cit.*)

PHENYL HYDROSULPHIDE, or *Phenyl-mercaptan*, $\text{C}^6\text{H}^5.\text{SH}$. According to Friedel & Crafts (*Compt. rend.* lxxxvi. 884) this compound is formed, together with phenyl sulphide, $(\text{C}^6\text{H}^5)^2\text{S}$, and diphenylene disulphide, $(\text{C}^6\text{H}^5)^2\text{S}_2$, by heating benzene with sulphur at 75° – 80° , in presence of aluminium chloride, and treating the

product with water. Its formation is explained on the supposition that the aluminium first reacts with the benzene and sulphur in such a manner as to form the compound $Al^3Cl^3.S.C^6H^5$, which is then decomposed by water, as shown by the equation:



The phenyl hydrosulphide thus obtained boiled at 170° – 173° , formed a crystalline compound with mercuric chloride, and was converted by iodine into phenyl bisulphide.

PHENYL SULPHIDE, $(C^6H^5)_2S$, also called *Thiobenzene* (iv. 417; vii. 941). Kraft (*Ber.* vii. 384, 1164) prepares this compound by converting thioaniline, $C^{12}H^{12}N^2S$ (vii. 1154), into a diazo-compound, and decomposing the latter with alcohol. As thus prepared, it boils at 288° – 289° (uncorr.), and is identical with the compound formed by the decomposition of sodium benzenesulphonate (Stenhouse, iv. 417), and with that which is produced by the dry distillation of the lead-salt of phenyl-mercaptan: $(C^6H^5S)^2Pb = PbS + (C^6H^5)_2S$ (Kekulé a. Szech, *Compt. rend.* lxiv. 752). The decomposition of sodium benzenesulphonate is best effected by Spring's method, which consists in treating the salt with phosphorus pentasulphide. The yellow-red oil thereby produced is decolorised by recently reduced copper-powder, and after two rectifications consists of nearly pure phenyl sulphide.

By adding phenyl sulphide to strong nitric acid, and reducing the resulting nitro-compound, thioaniline, $(C^6H^5.NH^2)_2S$, is obtained, melting at 106° , and crystallising from hot water in thin shining needles.

Bromophenyl Sulphide, $(C^6H^5Br)_2S$, produced by the action of bromine on phenyl sulphide, crystallises in nacreeous laminae melting at 109° – 110° . It may also be formed by cautiously heating the perbromide of diazothiobenzene. *Chlorophenyl Sulphide*, $(C^6H^5Cl)_2S$, produced by treating phenyl-sulphide with chlorine, or by the action of heat on the platinochloride of diazothiobenzene, resembles the bromine-compound and melts at 88° – 89° . *Iodophenyl Sulphide*, $(C^6H^5I)_2S$, may be prepared by Kekulé's method (vi. 267), which consists in heating phenyl sulphide with iodine and iodic acid in sealed tubes; also by adding dilute hydriodic acid to an aqueous solution of diazothiobenzene sulphate. It resembles the bromo- and chloro-derivatives, and melts at 138° – 139° .

Hydroxyphenyl Sulphide, $(C^6H^5.OH)_2S$, is obtained by the action of water on diazobenzene sulphate, and is precipitated from the alkaline solution by acids in shining laminae which melt at 143° – 144° .

Thiobenzenesulphonic acid, $(C^6H^5.SO^3H)_2S$, is easily obtained by dissolving phenyl sulphide in fuming sulphuric acid: its salts crystallise well (Kraft).

Phenyl Disulphide or *Diphenyl Disulphide*, $(C^6H^5)_2S^2$ (iv. 417), is decomposed by distillation, and, when boiled for about an hour and then distilled, yields the monosulphide, $(C^6H^5)_2S$, nearly pure, while a greasy substance remains behind. It is only by distillation from a retort in which the vapour cannot rise high, that the greater part of the disulphide can be made to pass over without decomposition. A thermometer with only its bulb immersed in the vapour then shows a temperature of 110° (Graebe, *Liebig's Annalen*, clxxiv. 189).

PHENYL-ACEDIAMINE, -ACETAMIDINE, or -ACETAMIMIDE, $C^6H^5.CH^2 \begin{smallmatrix} NH \\ \diagup \\ NH^2 \end{smallmatrix}$. See AMIDINES (p. 71).

PHENYL-ACETAZIDE, or *Acetyl-phenyl-hydrazide*, $C^6H^5.N^2H^2.C^2H^3O$. See HYDRAZINES (p. 1053).

PHENYL-ACETIC ACID, $C^6H^5.CH^2.CO.OH$, *α-Toluic acid*. See TOLUIC ACIDS.

PHENYL-ACETOTHIAMIDE, $CH^2(C^6H^5).CS.NH$. See THIAMIDES.

PHENYL-ACETYL-CARBAMIDE, $CON^2H^2(C^2H^3O)(C^6H^5)$. See ACETYL-CARBAMIDES (p. 393).

PHENYL-ACETYL-TRIOCARBAMIDE, $CSN^2H^2(C^2H^3O)(C^6H^5)$ (p. 400).

PHENYL-ALDEHYDINES (Ladenburg a. Engelbrecht, *Ber.* xi. 1653).

1. *Phenyl-benzaldehydine*, $C^6H^5(NC^6H^5)_2$, is prepared by agitating a dilute aqueous solution of orthophenylenediamine hydrochloride with benzaldehyde, recrystallising the hydrochloride which separates after some time from very dilute hydrochloric acid, and decomposing it with potash. It forms colourless six-sided prisms, insoluble in water, nearly insoluble in alkaline hydrates, easily soluble in alcohol and benzene; melts at 133° – 134° . Like other aldehydines it is a mono-acid base. The *hydrochloride*, $C^{20}H^{16}N^2.HCl$, prepared as above mentioned, forms colourless anhydrous

prisms, difficultly soluble in water, and decomposed on boiling, with separation of hydrochloric acid. The *platinochloride*, $(C^6H^5N^2.HCl)^2PtCl_4$, crystallises from dilute alcohol, with addition of hydrochloric acid, in golden-yellow needles. The *nitrate*, $C^{20}H^{16}N^2.HNO_3$, prepared by treating the hydrochloride with dilute nitric acid, forms colourless prisms, soluble in cold water. The *sulphate*, $C^{20}H^{16}N^2.H^2SO_4$, prepared by dissolving phenyl-benzaldehydine in hot dilute sulphuric acid, crystallises in small colourless shining plates. The *ethiodide*, $C^{20}H^{16}N^2.C^2H_5I$, obtained by heating the base with ethyl iodide in sealed tubes for some hours at 100° – 120° , separates from aqueous solution in well-formed crystals melting at 211° – 213° . The *methiodide*, $C^{20}H^{16}N^2.CH_3I$, prepared in like manner, crystallises in shining prisms.

Phenyl-furfuraldehydine, $C^6H^5(NC^3H^4O)^2$, is prepared like phenyl-benzaldehydine, substituting furfuraldehyde for benzaldehyde:



The resulting hydrochloride separates after a while in somewhat dark-coloured crystals, which may be purified by repeated crystallisation and treatment with animal charcoal. The base, separated from the solution by potash, may be purified by crystallisation from high-boiling ligroin, in which it is sparingly soluble, and separates from the solution in nearly colourless compact crystals melting at 95° – 96° .

Phenyl-furfuraldehydine is mono-acid. It dissolves very easily in alcohol, less easily in benzene and toluene, sparingly in ligroin, and is insoluble in water. It dissolves easily in dilute hydrochloric acid, forming a crystalline *hydrochloride* which appears to be decomposed by washing. The *platinochloride*, $(C^{16}H^{12}N^2O^2.HCl)^2PtCl_4$, crystallises in yellow laminae. The *nitrate*, $C^{16}H^{12}N^2O^2.HNO_3$, obtained by decomposing a very dilute solution of the hydrochloride with dilute nitric acid, crystallises in needles. The *acid sulphate*, $C^{16}H^{12}N^2O^2.H^2SO_4$, is obtained by dissolving the base in dilute sulphuric acid. The *methiodide*, $C^{16}H^{12}N^2O^2.CH_3I$, obtained by heating the base to 100° with methyl iodide, crystallises from hot water in yellowish prisms melting at 192° – 193° . The *ethiodide* was obtained only as a viscid mass showing but little tendency to crystallise.

Phenylanisaldehydine, $C^{22}H^{20}N^2O^2 = C^6H^5(NC^6H^4O)^2$, is prepared from anisaldehyde and a dilute aqueous solution of orthophenylenediamine hydrochloride with addition of a little alcohol. When separated from the hydrochloride by ammonia and repeatedly crystallised from alcohol, it forms stellate needles very soluble in hot alcohol, melting at 128.5° – 129° . The *hydrochloride* forms needles almost insoluble in water (Ladenburg a. Rugheimer, *Ber.* xi. 1660).

PHENYL-AMIDACETIC ACID, $C^6H^5.CH(NH^2).COOH$. This acid, prepared by the action of aqueous ammonia on phenylbromacetic acid, crystallises in pearly scales, which are insoluble in the usual neutral solvents, but dissolve in acids, and in solutions of the alkalis and alkaline carbonates. It sublimes with partial decomposition without melting. It unites with hydrochloric, nitric, sulphuric, oxalic, and phosphoric acids, forming crystalline compounds which are decomposed by water. With phosphorus pentachloride it yields benzaldehyde and a resinous product (Stöckenius, *Ber.* xi. 2002).

PHENYL-AMIDODICHLORACETATE, ETHYLIC,

$C^6H^5.NH.CCl_2.COOC^2H_5$, is formed by the action of phosphorus pentachloride at temperatures below 70° on ethylic phenyloxamate. See PHENYLOXAMIC ETHERS.

PHENYLAMINES. *Monophenylamine* or *Aniline*, and a large number of its derivatives, have already been considered in this volume (pp. 191–206 and 1305–1310).

Dichloranilines, $C^6H^3Cl_2.NH^2$ (p. 197).—Beilstein a. Kurbatow (*Ber.* xi. 1860) have completed the series of these bodies by the discovery of the 1 : 2 : 6 modification, $C^6.NH^2.Cl.H.H.H.Cl$, which is obtained by reduction of the corresponding nitro-dichlorobenzene (m. p. 71°). It crystallises in needles melting at 39° . Its acetyl-derivative melts at 173° . The following table exhibits the melting and boiling points of the six dichloranilines:—

	NH ²	Cl	Cl	Melting point	Acetyl-derivative.	
					Boiling point	Melting point
Consecutive	1	2	3	23.5°	252°	166.5
	1	2	6	39°	—	175°
	1	2	5	50°	251°	132°
Unsymmetrical	1	2	4	63°	245°	143°
	1	3	4	71.5°	272°	120.5°
Symmetrical	1	3	5	50.5°	260°	186.5°

Trichloranilines, $C^6H^3Cl_3.NH^2$. In addition to the two modifications described

at p. 147, Beilstein a. Kurbatow have obtained the consecutive modification 1 : 2 : 3 : 4 by chlorinating [1 : 2 : 4] dichloraniline in acetic acid solution. By exchange of NH^2 for Cl it is converted into consecutive tetrachlorobenzene. The physical characters of the three known modifications are shown in the following table:

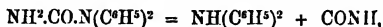
	NH^2	Cl	Cl	Cl	Melting point	Boiling point	Acetyl-derivative. Melting point
Consecutive	1	2	3	4	67.5°	292°	121°
Symmetrical	1	2	4	5	96.5°	270°	
Unsymmetrical	1	2	4	6	77.5°	260°	

Tetrachloranilines, $\text{C}_6\text{HCl}_4\text{NH}_2$. The modification $\text{NH}^2 : \text{Cl} : \text{Cl} : \text{Cl} : \text{Cl} : 1 : 2 : 3 : 4 : 6$, is obtained by chlorination of metachloraniline. It crystallises in needles melting at 88°. By the action of ethyl nitrite, it is converted into unsymmetrical tetrachlorobenzene (m. p. 50–51°). The acetyl-derivative melts at 173°–174°, and is not decomposed by heating with strong sulphuric acid.

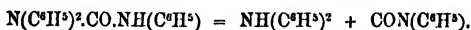
The modification 1 : 2 : 3 : 4 : 5 [NH^2 in 1], obtained by reduction of the corresponding nitrotetrachlorobenzene, forms crystals melting at 118°.

The modification 1 : 2 : 3 : 5 : 6, prepared in like manner, melts at 90°.

Diphenylamine, $\text{C}_{12}\text{H}_{11}\text{N} = \text{NH}(\text{C}_6\text{H}_5)_2$ (p. 207). This base is formed, together with cyanic acid (carbimide), by the dry distillation of unsymmetrical diphenyl-carbimide:



and in like manner, together with phenyl-carbimide, by distillation of triphenyl-carbimide (Michler, *Ber.* ix. 715):



Diphenylamine hydrochloride is obtained, together with the hydrochlorides of cresylamine and phenyl-cresylamine, by heating liquid toluidine to 280° for ten hours with aniline hydrochloride (Gerard a. Wilm, *Bull. Soc. Chim.* [2], xxv. 218).

Action of Chlorine on Diphenylamine.—A solution of diphenylamine in glacial acetic acid absorbs dry chlorine, forming tetrachlorodiphenylamine, $\text{NH}(\text{C}_6\text{H}_2\text{Cl}_4)_2$ (p. 209). Diphenylamine subjected to exhaustive treatment with chlorine and iodine (p. 1066), yields perchlorobenzene, C_2Cl_6 , probably together with free nitrogen (Rouff, *Ber.* ix. 1483).

Action of Bromine.—Tetra- and hex-bromodiphenylamine, $\text{NH}(\text{C}_6\text{H}_2\text{Br}_2)_2$, and $\text{NH}(\text{C}_6\text{H}_2\text{Br}_3)_2$, are produced by the action of bromine on diphenylamine dissolved in glacial acetic acid (p. 205). By exhaustive treatment with bromine containing iodine, diphenylamine is converted into octo- and deca-bromodiphenylamine. The former, $\text{NH}(\text{C}_6\text{H}_2\text{Br}_4)_2$, which is produced at 250°, crystallises in prisms, melts at 302°–305°, and dissolves with moderate facility in benzene, toluene, and chloroform. The latter, $\text{NH}(\text{C}_6\text{H}_2\text{Br}_5)_2$, formed at 310°, crystallises in white slender needles, remains unmelted at 310°, dissolves sparingly in benzene, toluene, and chloroform, and is nearly insoluble in alcohol and ether (Gessner, *Ber.* ix. 1505).

Nitro-diphenylamines.—A dinitro-diphenylamine, crystallising in red needles, and melting at 153°, is formed by the action of aniline on the trinitrobenzene obtained from paradinitrobenzene (p. 175), (Hepp, *Bull. Soc. Chim.* [2], xxx. 4).

Tetranitro-diphenylamine, $\text{C}_{12}\text{H}_7(\text{NO}_2)_4\text{N}$, isomeric with Austen's parapicryl-nitranilines (p. 199), is prepared by heating 1 pt. of diphenylamine dissolved in 40 pts. glacial acetic acid in a capacious flask with 3 to 5 pts. nitric acid, whereupon red fumes are evolved and the solution turns green. When the reaction is complete, excess of water is added, which throws down a yellowish flocculent precipitate, drying up to a dirty greenish-yellow powder, which becomes glutinous when heated, and solidifies to a brown resinous body when cold. It may be purified by boiling with dilute aqueous sodium carbonate, from which it separates on cooling in brownish-yellow flocculent masses melting at 150°–170°. Methyl-diphenylamine similarly treated yields the same body, and not a methyl-nitrodiphenylamine. The largest and purest yield is obtained by acting with 3 to 5 pts. nitric acid on 1 pt. of diphenyl-nitrosamine (p. 209) dissolved in 10 pts. of hot glacial acetic acid.

Tetranitrodiphenylamine, when pure, crystallises from glacial acetic acid in fine yellow needles or prisms melting at 192°. when more strongly heated in the air, it burns readily, but does not explode. It is soluble in alcohol, ether, and benzene, and, like its isomerides above mentioned, is easily dissolved by hot soda- or potash-ley, forming a solution of a fine scarlet colour, which on cooling deposits it in minute red-brown needles. It does not appear to yield an acetyl-derivative, even when heated in sealed tubes with acetyl chloride (Gnehm a. Wyes, *Ber.* x. 1318).

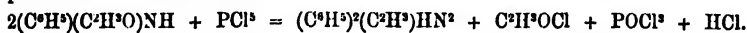
Dinitrotribromodiphenylamine, $C^{12}H^6Br^3N^3O^4 = C^{12}H^6Br^2(NO^2)^2N$, is formed, together with other compounds, by heating a solution of 1 pt. tetrabromodiphenylamine in 1 to 2 pts. nitric acid, whereupon large quantities of nitrogen tetroxide and bromine are evolved, and the solution on cooling deposits a crystalline mass, from which, by treatment with alcohol, glacial acetic acid, and caustic soda, different bodies may be separated, the portion soluble in alcohol yielding after repeated crystallisation thin glittering yellow plates of dinitrotribromodiphenylamine. This compound dissolves in ether with reddish-yellow, in benzene and chloroform with yellow colour, melts at $209^\circ-210^\circ$, and burns readily when strongly heated in the air (Gnehm a. Wyss).

Tetramidodiphenylamine, $C^{12}H^7(NH^2)^4N$.—Tetranitrodiphenylamine, reduced with zinc and dilute hydrochloric acid, yields an easily soluble colourless salt, from whose aqueous solution sodium hydrate precipitates a colourless, flocculent, basic substance, which in all probability consists of tetramidodiphenylamine, but has not been obtained in a state fit for analysis. Its solution in hydrochloric acid turns red-violet in the air; gives a violet colour with platinum chloride, gradually resolving itself into a dark precipitate; a dark violet with ferric chloride; a dark brown-red with zinc chloride; and with sodium nitrite a blue colour quickly turning red, and then resolving itself into a brown precipitate. By the addition of ammonia a colourless precipitate is formed, but on exposure to air this precipitate redissolves, and a splendid deep blue solution is formed, of very unstable character. Tetramidodiphenylamine is readily oxidised by exposure to the air, probably with formation of tetra-imidodiphenylamine, $NH[C^6H(NH)^2]^2$, the reaction being similar to that by which diimidonaphthol, $C^{10}H^{10}N^2O$, is converted into diimidonaphthol, $C^{10}H^8N^2O$ (vi. 857).

Methyl-diphenylamine, $N(CH^3)(C^6H^5)^2$.—This base, heated to 150° with fuming hydrochloric acid in a sealed tube, is resolved into methyl chloride and diphenylamine. Heated with nitric acid, as long as red vapours are given off, it yields a compound closely resembling Austen's diparapierylamine, $NH[C^6H^2(NO^2)^2]^2$ (p. 199), and perhaps identical therewith. The product, after washing with water, may be crystallised from alcohol or glacial acetic acid, and separates from the latter in yellow prisms melting at $233^\circ-234^\circ$. Its barium derivative, $BaN^2[C^6H^2(NO^2)^2]^2$, crystallises in rhombohedrons of a fine red colour; the ammonium derivative in red laminae. The same compound is formed by the action of nitric acid on diphenylamine itself, whence it appears that in the treatment of methyl-diphenylamine with nitric acid, the act of nitration is accompanied by a separation of the methyl-group (Gnehm, *Ber.* vii. 1399).

Methylene-diphenyldiamine, $C^{12}H^{14}N^2 = (C^6H^5)^2(CH^2)^2H^2N^2$, is formed by the action of methylene iodide on aniline. A gentle heat is required to start the action, which then takes place so violently that the entire mass becomes raised to the boiling point. In operating on considerable quantities, therefore, it is best to add the methylene iodide by drops to the aniline warmed in a water-bath. The thick crystalline pulp thus obtained is first distilled in a current of steam, then mixed with alkali and again distilled, whereupon there remains in the flask an oily substance, which must be separated from the alkaline solution by a tap-funnel and well washed with water. The oil which then remains is a strong base, which dissolves readily in acids. It does not, however, form crystallised salts, only the sulphate, $C^{12}H^{14}N^2.H^2SO^4$, being thrown down by alcohol from its aqueous solution as an indistinctly crystalline precipitate. The base prepared as above is analogous in all its chemical relations to the isomeric bases which Hugo Schiff obtained by the action of acetaldehyde and of ethylidene chloride on aniline (vi. 79, 922). *Dimethylene-diphenyldiamine* appears to be formed by treating aniline with excess of methylene iodide (Julie Lermontoff, *Ber.* vii. 1255).

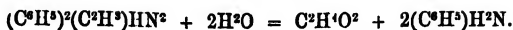
Ethenyl-diphenyldiamine, $(C^2H^3)(C^6H^5)^2HN^2 = C^2H^3 \begin{smallmatrix} N.C^6H^5 \\ \backslash NH.C^6H^5 \end{smallmatrix}$.—This base, which Hofmann obtained by the action of phosphorus trichloride on aniline mixed with acetanilide or acetyl chloride (vi. 585), is also formed by the action of phosphorus pentachloride on acetanilide:



Acetanilide (2 mols.) and PCl^5 (1 mol.) are mixed in a flask, whereupon the mass becomes hot, liquefies, and gives off hydrochloric acid, the evolution of which increases on heating the mixture with an inverted condenser attached to the flask. The solid residue is then to be shaken with water and precipitated with ammonia or potash, but it is only by repeated solution and precipitation that the base can be obtained crystalline and free from resin. When purified by recrystallisation from alcohol, it exhibits all the properties of the base described by Hofmann (E. Lippmann, *Ber.* vii. 241).

Ethenyldiphenyldiamine treated with reducing agents (tin or zinc and hydrochloric

acid), or sodium-amalgam in acetic acid solution, takes up $2\text{H}_2\text{O}$, and is resolved into acetic acid and aniline:



With *bromine* it forms ethenyl-dibromo-diphenyldiamine, which crystallises with some difficulty in broad laminæ. With fuming nitric acid it forms ethenyldinitrodiphenyldiamine nitrate, $\text{C}^{14}\text{H}^{12}(\text{NO}^2)^2\text{N}^2\cdot\text{HNO}^3$, which does not dissolve in water, alcohol, ether, alkalis, or acids. By prolonged boiling with water or acids, or prolonged heating with water in a sealed tube, this nitro-compound is converted, first into nitracetanilide and ultimately into paranitraniline (m. p. 141°). By reduction it is converted into paraphenylenediamine (R. Biedermann, *Ber.* vii. 539).

Ethylene-diphenyl-diamine, $\text{C}^2\text{H}^4(\text{C}^6\text{H}^5)^2\text{H}^2\text{N}^2$.—According to A. Gretilat (*Monit. Scient.* [3], iii. 383) this base, when prepared by treating ethylene bromide with a large excess of aniline (Hofmann's method, iv. 455), is always contaminated with diethylene-diphenyldiamine, $(\text{C}^2\text{H}^4)^2(\text{C}^6\text{H}^5)^2\text{N}^2$, which however may be separated by dissolving the whole in boiling concentrated acetic acid, and adding alcohol, whereupon the diethylene base separates in crystals.

The two free hydrogen-atoms in ethylenediphenyldiamine may be replaced by acid radicles, either fatty or aromatic. *Ethylenediacytyldiphenyldiamine* is a crystalline body easily soluble in alcohol and ligroin at the boiling heat, and still possessing basic properties; *ethylenedibenzoyldiphenyldiamine*, on the contrary, is destitute of basic properties (Gretilat).

Trichlorethylidene-diphenyldiamine, $\text{C}^{14}\text{H}^{12}\text{N}^2\text{Cl}^3 = \text{CCl}^3\cdot\text{CH}(\text{NH}\cdot\text{C}^6\text{H}^5)^2$, is formed by the action of aniline on anhydrous chloral. The action is violent, and the vessel must be cooled. The product is a thick liquid which soon becomes crystalline, and may be obtained by recrystallisation from alcohol in tabular crystals with well-developed faces. This compound dissolves readily in alcohol, ether, benzene, and chloroform, but is insoluble in water. It melts at 100° – 101° , and decomposes at 150° . By boiling with water, or by prolonged heating with alcohol, it is decomposed, with formation of phenyl isocyanide. The same product is formed by aqueous solutions of the alkalis, slowly in the cold, more rapidly when heated, and instantly with alcoholic potash. The first reaction is probably,



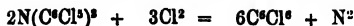
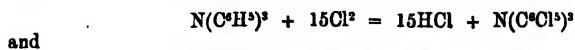
Chloroform cannot however be detected amongst the products of the reaction: it probably acts upon the aniline in such a manner as to produce another molecule of phenyl isocyanide.

Trichlorethylidene-diphenyldiamine does not appear to be a base: its alcoholic solution has a neutral reaction, and when treated with hydrochloric acid and platinum chloride yields the platinumchloride of aniline (Wallach, *Liebigs Annalen*, clxxiii. 349).

Diphenylamine-blue.—Willm. a. Girard (*Dingl. pol. J.* cxxi. 192) have obtained a blue dye-stuff by the following process: Pure formodiphenylamine (p. 208) is first prepared by heating 100 kg. diphenylamine with 30 kg. formic acid to 120° – 160° for twelve hours, and expelling the excess of formic acid by distillation. 1 kg. of this compound is then heated to 110° – 120° for twenty to twenty-four hours with 2 kg. oxalic acid; the product is poured into benzene; and the residue insoluble therein, after being freed by boiling water from adhering oxalic acid, is dried and dissolved in strong alcohol. This solution, heated with weak potash-ley, filtered, and mixed with hydrochloric acid, deposits the blue dyo-stuff; and this, when washed with water and treated at 40° – 50° with sulphuric acid, yields the corresponding sulphonic acid, which may be used directly as a dyeing liquid. The same colouring matter may be prepared from acetodiphenylamine. The corresponding dinaphthylamines, and the triamines formed from diphenylamine by introduction of methyl and benzyl instead of formyl and acetyl, are also said to yield the blue dye when treated as above; and similar blue colouring matters are said to be obtained by heating diphenylamine itself with dry oxalic acid, tartaric acid, &c.

Triphenylamine, $\text{N}(\text{C}^6\text{H}^5)^3$. On the formation of this base by the action of bromobenzene on potassium-aniline, see p. 209. It forms monoclinic crystals with the axial ratio $a : b : c = 0.9913 : 1 : 1.4119$. Angle $ac = 88^\circ 38'$. Observed forms 0P , $- \text{P}$, $+ \text{P}$, $+ \text{P} \infty$, $\infty \text{R} \infty$. The crystals are mostly twins according to 0P ; they are elongated in the direction of 0P and $- \text{P}$, and do not appear to be cleavable in any direction. Angle $- \text{P} : \infty \text{R} \infty = 51^\circ 16'$; $- \text{P} : \infty \text{P} = 26^\circ 19'$; $+ \text{P} : \infty \text{R} \infty = 50^\circ 38.5'$; $\infty \text{P} : 0\text{P} = 89.2'$. The plane of the optic axes is the plane of symmetry.

Triphenylamine, treated with *chlorine* and *iodine* (p. 1066), yields perchlorotriphenylamine, $\text{N}(\text{C}^6\text{Cl}^3)^3$; which by further chlorination is converted into perchlorobenzene:



(Ruoff, *Ber.* ix. 1483).

PHENYL-ARSENIC COMPOUNDS (Michaelis, *Ber.* viii. 1316; ix. 1566; x. 622; La Coste a. Michaelis, *ibid.* xi. 1883).

1. *Arsenious Dichlorophenide* or *Phenyl-dichlorarside*, $\text{C}^6\text{H}_5\text{AsCl}_2$, is formed by the action of arsenious chloride on mercury-diphenyl:



When three or four times the theoretical quantity of arsenious chloride is used, the action begins at ordinary temperatures, heat being evolved, and arsenious dichlorophenide produced, together with arsenious chlorodiphenide, $(\text{C}^6\text{H}_5)_2\text{AsCl}$, and mercuric chloride. The action is completed by heating the mixture for an hour, and the resulting liquid, when decanted from the solid sublimate and submitted to fractional distillation, yields the two phenyl-arsenic compounds above mentioned.

Arsenious dichlorophenide is also formed by heating arsenious chloride with benzene, $\text{C}^6\text{H}_6 + \text{AsCl}_3 = \text{HCl} + \text{C}^6\text{H}_5\text{AsCl}_2$. As thus produced, however, it is mixed with diphenyl formed by a secondary action, and cannot easily be separated; but its presence may be demonstrated by fusing the mass under water, and passing in chlorine to saturation, whereby arsenic tetrachlorophenide, $\text{C}^6\text{H}_5\text{AsCl}_4$, is first formed and then converted by the water into monophenylarsinic acid, $\text{C}^6\text{H}_5\text{AsO}(\text{OH})_2$ (La Coste a. Michaelis).

Arsenious dichlorophenide is a colourless, strongly refractive, not very mobile liquid, having a faint unpleasant smell in the cold, sharp and penetrating when warm, and exerting a violent corrosive action on the skin. It fumes in the air, and boils at 252° – 255° . It is not altered by boiling water, but alkalis dissolve it, forming salts which may be separated from the chloride of alkali-metal produced at the same time, by their solubility in absolute alcohol. The potassium salt, $\text{C}^6\text{H}_5\text{As}(\text{OK})_2$, heated with strong hydrochloric acid, is reconverted into arsenious dichlorophenide (Michaelis). By *bromine* in excess it is converted into arsenious bromodichloride, hydrogen bromide, and paradibromobenzene:

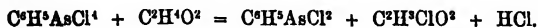


Arsenious Chlorodiphenide, or *Phenyl-cacodyl chloride*, $(\text{C}^6\text{H}_5)_2\text{AsCl}$, is the residue of higher boiling point obtained, as above mentioned, in the fractional distillation of the product of the action of arsenious chloride on mercuric phenide. When purified, it is a thick, oily, yellowish, non-fuming, and nearly scentless liquid, having a sp. gr. of 1.422 at 15° , and distilling unchanged at 333° , in an atmosphere of carbon dioxide. It is heavier than water, and is not decomposed thereby (Michaelis, *loc. cit.*)

Arsenic Trichlorodiphenide, or *Phenyl-cacodyl Trichloride*, $(\text{C}^6\text{H}_5)_2\text{AsCl}_3$, formed by direct combination of the last compound with chlorine, is a yellow solid resembling phosphorus pentachloride, but more stable in presence of water or damp air. It melts at 174° , and solidifies in crystals. It is decomposed by warm water, forming a liquid, probably an oxychlorophenide, which suffers further decomposition on boiling, yielding monophenylarsinic acid.

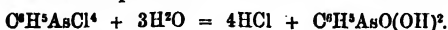
The *Bromodichlorodiphenide*, $(\text{C}^6\text{H}_5)_2\text{AsCl}_2\text{Br}$, a comparatively unstable body, is formed by direct combination of the dichlorophenide with bromine.

Arsenic Tetrachlorophenide, or *Phenyl-tetrachlorarside*, $\text{C}^6\text{H}_5\text{AsCl}_4$, formed by direct combination of arsenious dichlorophenide with chlorine, solidifies gradually at ordinary temperatures, quickly at 0° , to broad needles. It melts at 45° , and remains fluid for a long time after cooling. In moist air it is converted into arsenic oxydichlorophenide, $\text{C}^6\text{H}_5\text{AsOCl}_2$, and phenylarsinic acid, $(\text{C}^6\text{H}_5)\text{AsO}(\text{OH})_2$. It converts organic acids into chlorine-derivatives, acetic acid, for example, into monochloroacetic acid, being itself at the same time reduced to arsenious dichlorophenide:



It is not acted on by sulphur dioxide. When heated, especially in a stream of carbon dioxide, it is resolved into arsenious dichlorophenide and free chlorine. Heated to 150° in a sealed tube, it is resolved into arsenious chloride and monochlorobenzene.

Monophenylarsinic acid, $(\text{C}^6\text{H}_5)\text{AsO}(\text{OH})_2$, is formed by the action of excess of water on arsenic tetrachlorophenide:

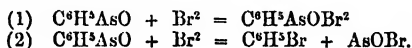


It is very soluble in water, and crystallises in long white needles, which soften at 158° , and are converted into the anhydride. Phenylarsinic acid forms normal salts only with the heavy metals, and these salts are mostly amorphous. Its solution neutralised with ammonia yields with silver nitrate a white precipitate of *silver phenylarsinate*, $C^6H^5AsO(OAg)^2$, sparingly soluble in water, easily soluble in ammonia and in nitric acid. With the alkalis and alkaline earths, the acid yields salts of the form $C^6H^5AsO(OH)OM'$; the *barium salt* crystallises in short radiating needles; the *copper salt* in pearly plates.

Monophenylarsenic Anhydride, $C^6H^5AsO_2$, obtained by heating the acid at 158° , is an amorphous powder, similar in constitution to nitrobenzene. On treating it or the corresponding acid with zinc and hydrochloric acid, the smell of an arsine becomes perceptible (La Coste a. Michaelis).

Diphenylarsinic or Phenylcacodylic acid, $(C^6H^5)^2AsO(OH)$, separates on cooling the filtrate obtained when the last-described body is decomposed by boiling water. It crystallises in slender needles, melts at 174° , dissolves with difficulty in cold, easily in hot water. The solution neutralised with ammonia gives, on addition of silver nitrate, a precipitate of *silver diphenylarsinate*, $(C^6H^5)^2AsO(OAg)$, soluble in ammonia and in nitric acid.

Arsenious Oxyphenide, C^6H^5AsO , obtained by the action of sodium carbonate on the dichlorophenide, crystallises from alcohol in crusts, smells like aniseed when cold, but when heated becomes very pungent, and attacks the mucous membranes of the nose. It is insoluble in water, melts at 120° , and is reconverted by aqueous hydrochloric acid into the dichlorophenide. When heated above its melting point, it is resolved into arsenious oxide and a high-boiling liquid, which solidifies on cooling and consists probably of triphenylarsine. Bromine acts violently on it, producing arsenic oxybromophenide and bromo-benzene:



Arsenic Oxychlorophenide, $C^6H^5AsOCl^2$, is formed by the action of water on arsenic tetrachlorophenide, but is more conveniently obtained by the action of chlorine on the oxyphenide, with which it combines very readily. It is a white crystalline body fuming in the air, and melting at about 100° . Water converts it into phenylarsenic acid; on heating it to 120° , it is resolved into arsenic oxychloride and chlorobenzene.

Arsenious Dibromophenide, $C^6H^5AsBr^2$, is obtained by heating the oxyphenide with concentrated hydrobromic acid, or by the action of arsenious bromide on mercury-diphenyl. It is a pale yellow liquid, having a faint smell, and boiling, not without decomposition, at 285° . It is not decomposed by water: bromine converts it into bromobenzene and arsenious bromide.

Diethylphenylarsine, $C^6H^5(C^2H^5)^2As$, is formed by adding a mixture of arsenious dichlorophenide and benzene or ether to zinc-ethyl. It is a refractive liquid having a faint but unpleasant smell, and boiling at 240° . It absorbs chlorine readily, forming crystalline arsenic dichlorodiethylphenide, $C^6H^5(C^2H^5)^2AsCl^2$. It also combines with ethyl iodide at 100° , forming the corresponding iodine-compound, $C^6H^5(C^2H^5)^2AsI^2$, which crystallises from water in thick needles.

Triphenylarsine or Arsenious Triphenide, $(C^6H^5)^3As$, is formed, together with $(C^6H^5)HgCl$ and $HgCl^2$, in the preparation of arsenious chlorodiphenide by heating arsenious dichlorophenide with mercuric phenide (p. 1552), and separates from the high-boiling residues left after the other products have passed over, in large rhombic plates. It is more easily prepared, however, by heating arsenious oxyphenide at 180° – 200° : $3(C^6H^5)AsO = As_2O^3 + (C^6H^5)^3As$. It melts at 58° – 59° , distils unchanged in an atmosphere of carbon dioxide at a temperature above 360° , dissolves easily in ether and benzene, sparingly in cold alcohol. It does not react with ethyl iodide at 100° .

Triphenylarsine Dichloride or Arsenic Dichlorotriphenide, $(C^6H^5)^3AsCl^2$, is obtained, by the action of dry chlorine on triphenylarsine, as a white powder, and crystallises from solution in benzene in colourless plates melting at 171° . At 280° it is resolved into monochlorobenzene and arsenious chlorodiphenide: $(C^6H^5)^3AsCl^2 = C^6H^5Cl + (C^6H^5)^2AsCl$. On treating it with boiling water or dilute ammonia, the chlorine-atoms are replaced by OH-groups, and triphenylarsine hydroxide, $As(C^6H^5)^3(OH)^2$, is formed, which crystallises from its aqueous solution in plates, from concentrated solutions in needles melting at 108° . Heated at 105° – 110° it loses 1 mol. of H_2O , and is converted into triphenylarsine oxide, $As(C^6H^5)^3O$.

Triphenylarsine forms with *mercuric chloride* the compound $\text{As}(\text{C}^6\text{H}^5)_3 \cdot \text{HgCl}_2$, a crystalline body, soluble in alcohol, but almost insoluble in water. It is not decomposed by aqueous potash in the cold, but on boiling the mercury is reduced to the metallic state, and $\text{As}(\text{C}^6\text{H}^5)_3(\text{OH})_2$ is formed. By the action of alcoholic potash in the cold it is resolved into mercuric oxide and triphenylarsine, which dissolves in the alcohol.

Diphenyl-ethylarsine, $(\text{C}^6\text{H}^5)_2\text{As}(\text{C}^2\text{H}_5)$, obtained by the action of zinc-ethyl on arsenious chlorodiphenide, is a colourless liquid, having a fruity smell, and boiling at 305° . It unites directly with chlorine, forming the solid dichloride, $(\text{C}^6\text{H}^5)_2\text{As}(\text{C}^2\text{H}_5)\text{Cl}_2$, which crystallises from benzene in long colourless needles. It combines with 1 mol. ethyl iodide at 100° , forming diphenyl-diethylarsonium iodide, $\text{As}(\text{C}^6\text{H}^5)_2(\text{C}^2\text{H}_5)_2\text{I}$. The corresponding chloride is uncrystallisable, but on mixing its solution with platinic chloride, the *platino-chloride*, $[\text{As}(\text{C}^6\text{H}^5)_2(\text{C}^2\text{H}_5)_2]^2\text{PtCl}_6$, is obtained as a yellow precipitate, slightly soluble in water, amorphous at first, but quickly becoming crystalline, and forming when dried, gold-yellow crystalline laminæ (La Coste a. Michaelis).

Monophenyltriethylarsonium Iodide, $(\text{C}^6\text{H}^5)\text{As}(\text{C}^2\text{H}_5)_3\text{I}$, is prepared by dropping zinc-ethyl diluted with 3 vols. benzene into a benzene-solution of the mixture of arsenious chlorodiphenide and diphenyl produced by the action of arsenious chloride on mercuric phenide. The benzene is then to be distilled off, and potash added, which precipitates monophenyl-diethylarsine and dissolves the diphenyl; and the arsine separated by filtration from the alkaline liquid, is heated in a sealed tube with ethyl iodide, whereby it is converted into phenyltriethylarsonium iodide, which may be freed from adhering diphenyl by recrystallisation from water.

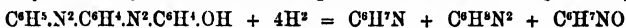
This iodide melts at 112° – 113° , and is resolved at a higher temperature in a stream of carbon dioxide into ethyl iodide and phenyl-diethylarsine. Heated for two or three hours at 110° in a sealed tube with silver oxide and water, it yields a strongly alkaline solution of the corresponding hydroxide, which remains on evaporation in the form of a syrup, and is easily converted into the chloride by neutralisation with hydrochloric acid. The chloride is uncrystallisable, but yields a platinochloride, $[\text{As}(\text{C}^6\text{H}^5)(\text{C}^2\text{H}_5)_2]^2\text{PtCl}_6$, in the form of a precipitate consisting of golden-yellow crystalline laminæ, which may be recrystallised from water (La Coste a. Michaelis, *Ber.* xi. 1884).

PHENYLAZODIETHYLAMIDOBENZOIC ACID,

$\text{C}^6\text{H}_5\text{N}=\text{N} \cdot \text{C}^6\text{H}_3(\text{COOH})\text{N}(\text{C}^2\text{H}_5)_2$. Syn. with AZOBENZENE-DIETHYLAMIDOCARBOXYLBENZENE, (p. 215). Similarly with regard to the corresponding methyl-compound.

PHENYLAZOPHENYLENE-AZOPHENYLENE HYDROXIDE,

$\text{C}^6\text{H}_5\text{N}_2 \cdot \text{C}^6\text{H}_4\text{N}_2 \cdot \text{C}^6\text{H}_4(\text{OH})$, formed from potassium-phenol and diazobenzene, is resolved by nascent hydrogen into aniline, paradiamidobenzene, and paramidophenol:



(Caro a. Schraube, *Ber.* x. 2230).

PHENYL-BENZENE SULPHAZIDE, $\text{C}^6\text{H}_5\text{N} \cdot \text{H}_2\text{SO}_2 \cdot \text{C}^6\text{H}_5$,

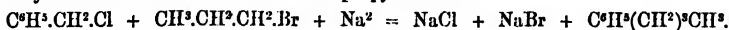
formed by the action of phenyl sulphochloride on phenyl-hydrazine in ethereal solution, crystallises in slender white needles, melting at 140° , slightly soluble in ether, benzene, and chloroform, easily in hot alcohol. By oxidation with mercuric oxide, it is converted into the diazo-compound, $\text{C}^6\text{H}_5\text{N}_2 \cdot \text{SO}_2 \cdot \text{C}^6\text{H}_5$, which Koenigs obtained (*Ber.* x. 1531) by the action of benzenesulphonic acid on diazobenzene (E. Fischer, *Liebig's Annalen*, cxc. 132).

PHENYL-BENZOYL-THIOCARBAMIDE, $\text{C}^6\text{H}_5\text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}^6\text{H}_5$.

See CARBAMIDES (p. 400).

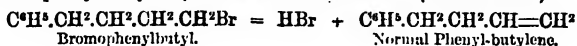
PHENYL-BUTYLS or BUTYL-BENZENES, $\text{C}^{10}\text{H}^{14} = \text{C}^6\text{H}_5 \cdot \text{C}^4\text{H}_9$.

Normal Phenyl-butyl, $\text{C}^6\text{H}_5 \cdot (\text{CH}_2)_3 \cdot \text{CH}_3$, is obtained by the action of sodium on a mixture of benzyl chloride or bromide and normal propyl bromide:



The reaction may be carried out on the sand-bath without the use of any diluent (Radziszewski, *Ber.* ix. 260°). According to Balbiano (*ibid.* x. 296), normal phenyl-butyl is also formed by the action of sodium on a mixture of bromobenzene and normal butyl bromide.

Normal phenyl-butyl is a colourless, strongly-refractive, fragrant liquid, having a density of 0.8622 at 16° , and boiling at 180° (cymene boils at 175° – 176°). Heated with bromine it yields a substitution-product, which when distilled gives off hydrogen bromide and yields two hydrocarbons, one of which is readily polymerised, while the other (normal phenyl-butylene) distils without alteration (Radziszewski):



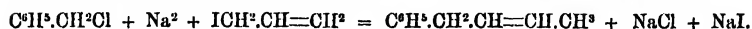
Bromophenylbutyl.

Normal Phenyl-butylene.

Phenyl-isobutyl, $C^6H^5.CH^2.CH(CH^3)^2$.—Of this hydrocarbon there are two modifications, distinguished as α and β . The α -modification is obtained in small quantity by the action of sodium on an ethereal solution of the bromides cooled by a mixture of ice and salt. It is a transparent colourless liquid, having a fragrant but very pungent odour, a specific gravity of 0.8577 at 0° , and boiling at 159° – 161° (J. Riess, *Ber.* iii. 779); sp. gr. 0.89 at 15° , boiling point 167.5° (Radziszewski, *ibid.* ix. 260). By oxidation with chromic acid mixture, it is converted into benzoic acid. Its *bromo*- and *nitro*-derivatives are uncrystallisable; the *monamido*-derivative does not form crystallisable salts. The *sulphonic acid* crystallises in fine, transparent and colourless, rhombic needles; its *barium salt* in fine white laminae easily soluble in water and dilute alcohol, sparingly in absolute alcohol and in ether (Riess).

β -*Phenyl-isobutyl* is formed, with brisk reaction, on treating an ethereal solution of phenyl-bromethyl, $C^6H^5.CHBr.CH^3$, with zinc-ethyl. It is a colourless liquid, having a specific gravity of 0.8726 at 16° , and boiling at 170° – 172° (Radziszewski, *loc. cit.*)

PHENYL-BUTYLENE, $C^{10}H^{12} = C^6H^5(C^4H^3)$. The hydrocarbon of this composition (b. p. 176° – 178°), which Aronheim obtained in 1872 by mixing benzyl chloride with allyl iodide in ethereal solution (vii. 495), is now regarded by him as constituted according to the formula $C^6H^5.CH^2.CH=CH.CH^3$, and supposed to be formed (on the hypothesis of molecular transposition) according to the equation :



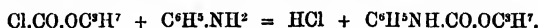
Its *bromide*, $C^{10}H^{12}Br^2$, is converted by oxidation with nitric acid into the phenyl-monobromopropionic acid described by Glaser (vi. 470, 962); but the success of the reaction appears to depend on peculiar conditions (Aronheim).

Normal phenyl-butylene, $C^6H^5.C^4H^3$, produced as above mentioned, by distillation of normal bromophenyl-butyl, boils at 186° , and forms with bromine the compound $C^{10}H^{12}Br^2$, which crystallises in white needles having a silky lustre, and melting at 70° – 71° . On distilling this dibromide with lime, a mass is obtained, which after purification exhibits the odour, crystalline form, and melting point of naphthalene (Radziszewski, *Ber.* ix. 260).

PHENYL-CACODYLIC ACID, syn. with DIPHENYL-ARSINIC ACID (p. 1553).

PHENYL-CACODYL-CHLORIDES (Di- and Tri-), syn. with ARSENIOS and ARSENIC CHLORODIPHENIDES respectively (p. 1552).

PHENYL-CARBAMATE, PROPYLIC, $C^6H^5.NH.CO.OCC^3H^7$, is formed by the action of aniline in ethereal solution on propyl chlorocarbonate :



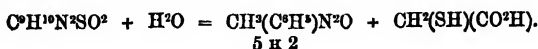
It crystallises in slender needles, easily soluble in alcohol, less soluble in water, melting at 57° – 59° (H. Römer, *Ber.* vi. 1101).

PHENYL-CARBAMIDE, $NH^2.CO.NH(C^6H^5)$. On the crystalline form and other physical characters of this compound, see CARBAMIDES (p. 390).

Diphenyl-carbamide.—The symmetrical modification of this compound, $(C^6H^5)HN.CO.NH(C^6H^5)$, or carbanilide, is formed by the action of water on dibenz-hydroxamic acid. See HYDROXAMIC ETHERS (p. 1080).

PHENYL-CARBODIIMIDOTHIAcETIC ACID, $C^6H^5N^2SO^2 =$

$C^6H^5.NH.C \begin{smallmatrix} \nwarrow NH \\ \nearrow S.CH^2.COOH \end{smallmatrix}$ This acid is formed by the action of monochloroacetic acid on aniline thiocyanate, or a mixture of a metallic thiocyanate with aniline. The best yield is obtained by heating 1 mol. aniline dissolved in twice its weight of absolute alcohol on the water-bath with 1 mol. ammonium thiocyanate and 1 mol. chloroacetic acid. A brisk reaction then sets in, attended with evolution of gas, and crystals separate, increasing in quantity as the liquid cools: they may be purified by repeated crystallisation from absolute alcohol and boiling with ether. The compound thus obtained dissolves easily in hot water, alcohol, and acetic acid, sparingly in ether, and crystallises in flattened prisms, apparently orthorhombic, which melt at 148° – 152° . Its aqueous solution has an acid reaction, but no salt or ethyl-compound of it has yet been obtained. The solution is coloured deep yellow by iron salts, and decomposed by prolonged boiling with alkalis and acids. Boiled for several hours with sulphuric acid (20 per cent.) it yields phenyl-carbamide and thioglycollic acid :



The corresponding *paratolyl-compound*, $C^{10}H^{12}N^2SO^2$, obtained in like manner by heating paratoluidine with ammonium thiocyanate and chloracetic acid, melts at 176° – 182° , and is resolved by boiling with sulphuric acid into thioglycollic acid and tolyl-carbamide (Jäger, *J. pr. Chem.* [2], xvi. 1).

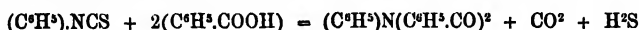
PHENYL-CHLORACETAMIDE, $C^6H^5.NH.C^2H^2ClO$. See ACETAMIDES (p. 5).

PHENYL-CRESYLAMINES, $C^6H^4(CH^3).NH(C^6H^5)$. See TOLUIDINES.

PHENYL-CROTONIC ACID, $C^{10}H^{10}O^2 = C^6H^5.C^2H^4.CO^2H$. See CINNAMIC ACID, HOMOLOGUES OF (p. 500).

PHENYL-CYMYL-CARBAMIDE, $C^6H^5.NH.CO.NH.C^{10}H^{12}$. See CARBAMIDES (p. 392).

PHENYL-DIBENZAMIDE, $(C^6H^5)N(C^7H^5O)^2$, analogous to Hofmann's phenyl-diacetamide (vii. 946), is formed by the action of benzoic acid on phenylthiocarbimide at 130° – 150° :



(Losanitsch, *Ber.* vi. 176).

PHENYL-DIETHYL-AZONIUM BROMIDE, $C^6H^5.N^2H^2(C^2H^5).C^2H^5Br$. See HYDRAZINES (p. 1051).

PHENYL-DIPHENYLENE SULPHIDE, $C^{16}H^{12}S = \begin{array}{c} C^6H^5 - C^6H^5 \\ | \quad \diagup \\ C^6H^5 \quad S \end{array}$. This

appears to be the principal constituent of the higher-boiling portion of the crude diphenylene sulphide which Graebe obtained by passing the vapour of phenyl sulphide, $(C^6H^5)S$, through a red-hot tube filled with iron nails (p. 669).

PHENYLENE-CARBAMIDE, $C^6H^4(NH.CO.NH^2)^2$. See CARBAMIDES (p. 392).

PHENYLENE-DIAMINES, $C^6H^4N^2 = NH^2.C^6H^4.NH^2$. *Diamidobenzenes*.—These bases are obtained by the action of reducing agents on the corresponding dinitrobenzenes and nitroamidobenzenes (nitranilines), and by dry distillation of the corresponding diamidobenzoic acids (iv. 480; vii. 946). The following are their melting and boiling points, those of the *meta*- and *para*-modifications according to Hofmann, those of the *ortho*-modification according to Griess:

	Ortho	Meta	Para*
Melting points	99°	63°	147°
Boiling points	252°	287°	267°

Ortho-phenylene-diamine is also produced. (a). From ortho-nitrobromobenzene (p. 176), by heating that compound with alcoholic ammonia, whereby it is converted into orthonitraniline, and reducing the latter with tin and hydrochloric acid (Zincke a. Sintonis, *Ber.* vi. 637). (b). From metabromorthonitraniline, $C^6H^4NH^2.NO^2.H.H.Br.H$ (p. 199), by reduction with tin and hydrochloric acid, and treatment of the resulting bromodiamido-benzene with sodium-amalgam (Wurster, p. 201).

Orthophenylenediamine is converted, by the action of a dilute solution of potassium nitrite slightly acidulated with sulphuric acid, into amidazo-phenylene, $C^6H^4N^2$, which crystallises in white nacreous needles melting at 98.5° (Ladenburg, *Ber.* ix. 219).

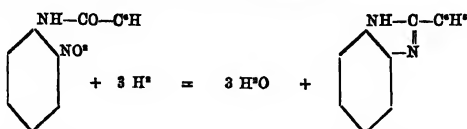
Methenyl-o-phenylenediamine, $C^7H^6N^2 = C^6H^4 \begin{array}{c} NH \\ \diagup \quad \diagdown \\ N \end{array} CH$, is obtained by heating *o*-phenylene diamine with formic acid for four hours in a flask connected with an upright condenser. It is a white crystalline body which melts at 167° , and boils at 360° , dissolves in alcohol, water, and acids, and is precipitated from acid solutions on the addition of ammonia. The hydrochloride, sulphate, nitrate, and acetate are extremely soluble in water. The *hydrochloride* has the composition $C^7H^6N^2.HCl + H^2O$. The *platinochloride*, $(C^7H^6N^2.HCl)^2PtCl_4$, crystallises with 2 mols. water, which it gives off at 160° . The *aurochloride*, $C^7H^6N^2.HCl.AuCl_3$, separates from solution in dilute hydrochloric acid in feathery groups of yellow anhydrous crystals (E. Wundt, *Ber.* xi. 826).

* The base melting at 63° was formerly regarded as the *para*-, and the base melting at 147° as the *meta*-modification (vii. 947); but recent investigation having shown that ordinary dinitrobenzene, from which the former is derived, is a *meta*-compound (p. 175), it follows that the original designations of these two bases must be reversed.

Ethenyl-o-phenylene-diamine, $C^6H^6N^2 = C^6H^4 \begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C^2H^2$, prepared by boiling orthophenylenediamine with glacial acetic acid, melts at 175° , and distills without decomposition (Ladenburg, *Ber.* viii. 677).

Propenyl-phenylenediamine, $C^6H^{10}N^2 = C^6H^4 \begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C^3H^3$, prepared by heating propionic acid with orthophenylenediamine, melts at 168.5° – 169° , and boils above 360° . It is very soluble in alcohol, ether, and acids, and is deposited from its aqueous solution in thin plates. All its salts, except the picrate, are very soluble in cold water. The picrate, $C^6H^{10}O^2.C^6H^2(NO^2)^3.OH$, is deposited from a hot saturated aqueous solution, on cooling, in yellow needles (Wundt).

Anhydrobenzoyl-phenylenediamine, $C^{10}H^{10}N^2 = C^6H^4 \begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C.C^4H^3$, is formed by the action of hydrogen on orthonitrobenzanilide:



Fuming nitric acid converts it into a mononitro-derivative, which is but feebly basic, melts at 196° , dissolves easily in hot alcohol and glacial acetic acid, and crystallises from the alcoholic solution in granular groups of needles. With tin and hydrochloric acid, it yields the bi-acid base, $C^{12}H^{12}N^2 = NH^2.C^6H^4 \begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C.C^6H^5$, which separates from a saturated alcoholic solution in dense white granules, melting at 245° (Hübner a. Stöver, *Ber.* vii. 1314).

Amylanhydrobenzoyl-phenylenediamine, $C^{18}H^{18}N^2 = C^6H^4 \begin{smallmatrix} \text{N.C}^5\text{H}^{11} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C.C^6H^5$, is obtained as a hydriodide by heating the preceding compound with excess of amyl iodide at 180° (another compound crystallises in white laminae, insoluble even in hot water, being formed at the same time). The free base crystallises from alcohol in microscopic rhombic plates, melting at 270° . Its salts are crystallisable (Sennewald, *Ber.* ix. 775).

Ethylanhydrobenzoyl-phenylenediamine, $C^8H^8 \begin{smallmatrix} \text{N.C}^2\text{H}^5 \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} > C.C^6H^5$, is formed in like manner together with another compound. It is moderately soluble in water; its hydrochloride and basic sulphate crystallise in needles (Sennewald).

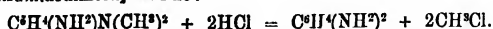
Metaphenylenediamine is formed by reduction of ordinary dinitrobenzene, and by distillation of either of the three metadiamidobenzoic acids (p. 273). It occurs also as a bye-product in the manufacture of aniline (p. 210). Boiled for five or six hours with oxalic acid and alcohol, it is converted into phenylene-oxamic acid, $NH^2.C^6H^4.NH.CO.COOH$ (p. 1457).

Chloro-m-phenylenediamine, $C^6NH^2.H.NH^2.Cl.H^2$, melting at 86° , is formed by the action of tin and hydrochloric acid on the corresponding dinitrochlorobenzene (m. p. 50°), p. 183 (Beilstein a. Kurbatow, *Ber.* xi. 1939).

Nitrochloro-m-phenylenediamine, $C^6NH^2.NO^2.NH^2.H.Cl.H$, is formed by the action of alcoholic ammonia on nitrochlorobenzene, $C^6.Cl.NO^2.Cl.H.Cl.H$ (m. p. 68°), (Beilstein a. Kurbatow, *Ber.* xi. 1978).

Tetramethyl-m-phenylenediamine, $(CH^3)^2N.C^6H^4.N(CH^3)^2$, is formed by the action of methyl alcohol and hydrochloric acid on metaphenylenediamine, and separates from the resulting solution on addition of caustic soda, as an uncrystallisable oil having a peculiar odour and boiling at 256° (corr.). Its hydrochloride forms hygroscopic crystals. The free base unites with methyl iodide to form the compound $C^6H^4[N(CH^3)^2]^2.CH^3I + H^2O$, which dissolves freely in water, but is less soluble in alcohol; it melts at 192° with decomposition into its constituents. Tetramethylmetaphenylenediamine forms a liquid dibromo-compound, and is converted by the action of nitric acid on its acetic acid solution into the nitrosamine of trinitrotrimethylmetaphenylenediamine, $C^6H(NO^2)^3N^2(CH^3)^3NO$, a yellow crystalline body, which dissolves in alcohol and in benzene, and melts at 132° (Wurster a. Morley, *Ber.* xii. 1814).

Paraphenylenediamine is formed: a. By the action of dry hydrogen chloride at 180° on paramidodimethylaniline:



b. As hydrochloride, together with the tin salt of diamidodiphenylcarbamide,

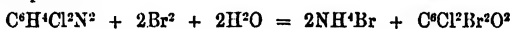
$\text{CO}(\text{NH} \cdot \text{C}^6\text{H}^4 \cdot \text{NH}^2)^2 \cdot 2\text{HCl} \cdot \text{SnCl}_2$, by the action of tin and hydrochloric acid on the nitro-product (chiefly dinitrocarbanilide), obtained by the action of nitric acid on carbanilide. The hydrochloride of the phenylene-diamine is more soluble than the tin salt just mentioned (H. Schiff, *Liebig's Annalen*, clxxxix. 157). γ . By reduction of nitraniline from nitracetanilide with tin and hydrochloric acid (Biedermann a. Ledoux, p. 210).

Paraphenylene-diamine melts, according to Hofmann, at 140° , but according to Biedermann a. Ledoux, the perfectly pure base obtained by dry distillation of the hydrochloride with sodium carbonate, melts at 147° (p. 210).

Reaction with Calcium Hypochlorite.—When a solution of paraphenylenediamine hydrochloride slightly acidulated with hydrochloric acid is quickly stirred into an excess of a solution of bleaching powder (1 mol. of the hydrochloride to 3 mols. chlorine), a yellowish-white precipitate separates out, having the composition of dichlorodiimidobenzene, $\text{C}^6\text{H}^4\text{Cl}_2\text{N}^2 = \text{C}^6\text{H}_2(\text{Cl})_2(\text{NH})^2$. This compound is soluble in alcohol, ether, benzene, and glacial acetic acid, sparingly in hot water. When slowly heated in an oil-bath it detonates at 124° , but if rapidly heated it may be melted without decomposition. By the action of reducing agents it is reconverted into phenylenediamine hydrochloride. Hydrochloric acid of sp. gr. 1.2 converts it into a substance which has the composition $\text{C}^6\text{H}^4\text{Cl}_2\text{N}^2$ or $\text{C}^6\text{H}^6\text{Cl}_2\text{N}^2$; crystallises in pale-red needles; is insoluble in water and in cold hydrochloric acid, but dissolves freely in alcohol, benzene, ether, and glacial acetic acid; and is converted by nitric acid into tetrachloroquinone (chloranil), which is likewise produced by passing chlorine into a solution of paraphenylene-diamine in glacial acetic acid.

Hydrobromic acid appears to act on dichlorodiimidobenzene similarly to hydrochloric acid.

Dichlorodiimidobenzene, dissolved in glacial acetic acid and treated with bromine and water, is converted into dichlorodibromoquinone, $\text{C}^6\text{Cl}_2\text{Br}_2\text{O}^2$, which separates in rhombic plates:



(A. Kraus, *Ber.* xii. 47).

Dinitro-p-phenylenediamines, $\text{C}^6\text{H}^2(\text{NO}_2)^2(\text{NH}^2)^2$.—Biedermann a. Ledoux obtained a body of this composition by heating diaceto-p-phenylenediamine with alcoholic ammonia: it crystallised in red needles melting at 294° (p. 210). Another modification (distinguished as β), first observed by Clemm (*J. pr. Chem.* [2], i. 145), is produced by heating [1 : 2 : 4 : 6] trinitraniline (picramide, p. 198) with alcoholic ammonium sulphide at 130° . It crystallises in long slender red needles melting at 210° . It unites with hydrochloric acid, forming the compound $\text{C}^6\text{H}^4\text{N}^4\text{O}_4 \cdot \text{HCl}$, which however is decomposed by water. By the action of acetyl chloride it is converted into the *diacetyl-compound*, $\text{C}^6\text{H}^4(\text{C}^2\text{H}_3\text{O})^2\text{N}^4\text{O}_4$, which crystallises in slender bright yellow needles melting at 245° (Norton a. Elliott, *Ber.* xi. 327).

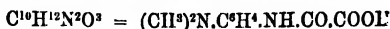
DIMETHYLPARAPHENYLENEDIAMINE, $\text{C}^6\text{H}^{12}\text{N}^2 = \text{NH}_2 \cdot \text{C}^6\text{H}^4 \cdot \text{N}(\text{CH}_3)^2$ [$\text{NH}_2 : \text{N}(\text{CH}_3)^2 = 1 : 4$]. This base is prepared by the action of tin and hydrochloric acid on nitrosodimethylaniline (p. 1309), (Schraube, *Ber.* viii. 616; Wurster, *ibid.* xii. 522), or on tetramethylidamidazoxybenzene (Schraube); also by similar reduction of nitrodimethylaniline (A. Weber, *ibid.* x. 760). To obtain the pure base, Wurster gradually adds the tin salt, which is the immediate product of the reaction, to an excess of warm soda-ley, whereupon the base separates as a brown oil which may be dried over calcium chloride and distilled, the distillate on cooling depositing the base in crystals, which may be pressed between paper and dissolved in a small quantity of warm benzene. On cautiously adding warm petroleum ether to this solution, an oil separates out containing all the impurities, and on subsequently adding cold petroleum-ether, the pure dimethyl-phenylenediamine separates in long white needles resembling asbestos.

Dimethylparaphenylenediamine melts at 41° and boils at 257° . When pure it does not change on exposure to the air, but the impure base turns red or violet. It dissolves freely in water, alcohol, benzene, and chloroform, but is less soluble in ether and in light petroleum.

When a 10 per cent. solution of bromine in glacial acetic acid is added to a somewhat more dilute solution of dimethylparaphenylenediamine in the same solvent, a green substance is precipitated, which has the composition $\text{C}^6\text{H}^{11}\text{N}^2\text{Br}$. The precipitate must be thoroughly washed with glacial acetic acid and with anhydrous ether, and may be rapidly recrystallised from hot alcohol, from which it is deposited in green scales, having a metallic lustre and melting at 146° . The aqueous and alcoholic solutions of this substance exhibit a deep red colour, which is destroyed by exposure to the air or by the addition of sulphurous acid (Wurster a. Sendtner, *Ber.* xii. 1803).

Acetyl-dimethyl-paraphenylenediamine, $(\text{CH}_3)_2\text{N}.\text{C}_6\text{H}_4.\text{NH}(\text{C}_2\text{H}_3\text{O})$, prepared by treating the base with acetic anhydride at ordinary temperatures, or boiling it with glacial acetic acid, crystallises in white needles or plates, melts at 130° , boils with slight decomposition at 355° , and dissolves in benzene, alcohol, and hot water (Wurster).

Dimethylparaphenylenediamine-oxamic acid,



The ethylic ether of this acid is obtained, together with diparamido-dimethylphenyl-oxamide, by heating 1 mol. dimethylparaphenylenediamine with rather more than 1 mol. ethyl oxalate, treating the product with ether to remove the excess of ethyl oxalate, and digesting the residue in warm alcohol, which dissolves out the oxamic ether, and leaves the phenyl-oxamide.

The acid, $\text{C}^1\text{O}^1\text{H}^{12}\text{N}^2\text{O}^3$, crystallises in grey needles or plates which dissolve freely in boiling water, but only sparingly in boiling alcohol, and melt with decomposition at 192° . The *ethylic ether* crystallises in yellow needles or plates, melts at 117° , dissolves in hot water and hot alcohol, also in acids, forming crystalline salts. On adding alcoholic ammonia to an alcoholic solution of this ether, *monoparamido-dimethylphenyl-oxamide*, $(\text{CH}_3)_2\text{N}.\text{C}_6\text{H}_4.\text{NH}.\text{CO}.\text{CONH}_2$, crystallises out. This substance melts at 257° – 259° , dissolves in hot benzene, and unites with acids forming crystalline salts soluble in hot water (Sendtner, *Ber.* xii. 530).

Diparamidodimethylphenyl-oxamide, $[\text{CONH}.\text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2]^2$, forms a yellow crystalline powder which does not melt when heated to 270° . It is soluble in boiling benzene and chloroform. Its salts dissolve readily in water.

When a solution of ethylic dimethylparaphenylenediamine-oxamate in dilute hydrochloric acid is treated with *sodium nitrite*, a yellowish-red nitro-product, $(\text{CH}_3)_2\text{N}.\text{C}_6\text{H}_4.\text{N}(\text{NO}_2).\text{NH}.\text{CO}.\text{COOC}_2\text{H}_5$, collects on the surface. This substance, when recrystallised from acetic acid, forms red needles melting at 152° , freely soluble in benzene, less soluble in ether and in boiling water. On reduction with tin and hydrochloric acid, it yields oxalic acid and dimethyltriamidobenzene, $\text{C}_6\text{H}_3\text{N}(\text{CH}_3)_2.\text{H}.\text{NH}_2.\text{NH}_2.\text{H}_2$, which crystallises in colourless prisms melting at 42° – 44° , boils at 298° , dissolves in water and in petroleum-ether, and forms an acetyl-derivative crystallising from water in transparent prisms or plates which contain 1 mol. H_2O , and begin to melt at 82° , resolidify at 120° , and then melt at 153° . From benzene anhydrous crystals are obtained which melt at 153° (Wurster a. Sendtner, *Ber.* xii. 1804).

Dimethylparaphenylenediamine-carbamides. — The dicarbamide, $\text{CO}[\text{NH}.\text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2]^2$, is formed by heating 1 pt. of urea with 4 pts. of dimethylparaphenylenediamine at 130° – 150° for three hours. The crude product is washed with alcohol, and purified by conversion into the sulphate. The dicarbamide crystallises in long needles soluble in boiling acetone. It melts with decomposition at 262° . The *sulphate*, $\text{C}^1\text{H}^{12}\text{N}^4\text{O}.\text{H}_2\text{SO}_4$, is sparingly soluble in water; the *hydrochloride*, $\text{C}^1\text{H}^{12}\text{N}^4\text{O}.\text{HCl}$, is very soluble.

The monocarbamide, $\text{NH}_2.\text{CO}.\text{NH}.\text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2$, obtained by mixing solutions of potassium cyanate and dimethylparaphenylenediamine, forms large white needle-shaped crystals (melting at 179°), soluble in boiling water. The sulphate and hydrochloride are easily soluble (F. Binder, *Ber.* xii. 535).

The thiodicarbamide, $\text{CS}[\text{NH}.\text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2]^2$, obtained by boiling the diamine with carbon bisulphide, is a white crystalline powder, melting at 186.5° , soluble in hot benzene and hot alcohol. The *hydrochloride*, $\text{C}^1\text{H}^{12}\text{N}_4\text{S}.\text{HCl}$, is a white powder soluble in alcohol. The *acetyl-derivative*, obtained by heating the thiocarbamide with acetic anhydride on the water-bath and then adding alcohol, crystallises on cooling in white nacreous laminae melting at 71° (A. Baur, *Ber.* xii. 533).

Sulphuretted Colouring Matters derived from Dimethylparaphenylenediamine (A. Koch, *Ber.* xii. 592–595). — The blue colouring matter formed by treating dimethylparaphenylenediamine first with sulphuretted hydrogen and then with ferric chloride (p. 211) may be precipitated by zinc chloride, and purified by dissolving it in water and reprecipitating with zinc chloride. When hydrochloric acid is added to an aqueous solution of this blue compound, dark blue plates having a strong metallic lustre slowly separate out. These crystals, after drying at 110° , have the composition $\text{C}^1\text{H}^{10}\text{N}_4\text{S}.\text{HCl}$, with $1\frac{1}{2}$ to 4 mol. H_2O . This compound is soluble in water and alcohol; it is bleached by reducing agents, and precipitated by potassium dichromate, zinc chloride, and mercuric chloride. When sulphuretted hydrogen is passed through its ammoniacal solution, a yellow precipitate is formed, which turns green on exposure to the air.

On evaporating the liquid from which the original blue colouring matter has been precipitated by zinc chloride, bronze-coloured needles separate out, having the composition $C^{16}H^{18}N^4S^4.2HCl.ZnCl^2 + 2H^2O$. This substance is soluble in water and alcohol. It is precipitated by mercuric chloride, and bleached by alkalis.

The formation of the original blue compound is represented by the equation $2C^6H^{12}N^2 + H^2S + O = C^{16}H^{18}N^4S + 4H^2O$, and that of the bronze-compound by the equation $2C^6H^{12}N^2 + 4H^2S + O = C^{16}H^{18}N^4S^4 + 7H^2O$ (A. Koch, *Ber.* xii. 592).

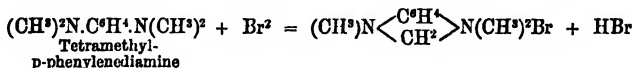
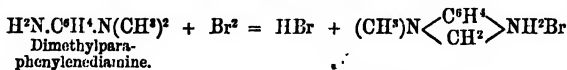
TETRAMETHYLPARAPHENYLENE-DIAMINE, $(CH^3)^2N.C^6H^4.N(CH^3)^2$, which Hofmann obtained, together with other products, by the action of methyl iodide on the dimethylated base (iv. 481) is also produced by heating a mixture of dimethylparaphenylenediamine with methyl alcohol and hydrochloric acid in sealed tubes, first at 180° , afterwards at 200° . On adding soda to the crude product, an oil separates out, which, when purified by distillation and crystallisation from dilute alcohol, deposits tetramethylparaphenylenediamine in white plates. This base melts at 51° , and boils without decomposition at 260° ; dissolves in hot water and the other ordinary solvents. Oxidising agents colour its solutions deep blue. The hydrochloride, sulphate, and platinochloride dissolve readily in water (Wurster, *Ber.* xii. 526).

By the action of *bromine* on a solution of tetramethylparaphenylenediamine in acetic acid, an unstable blue compound, $C^{16}H^{14}N^2$, is formed, which may be obtained in the form of a microscopic crystalline precipitate by adding ether to the mixture; its solution in water and in alcohol has a deep blue colour, which is destroyed by sulphurous acid. The substance can also be obtained as ferrocyanide, by adding potassium ferricyanide to tetramethylphenylenediamine sulphate, $C^{16}H^{16}N^2 + H^6Fe^3Cy^{12} = C^{16}H^{14}N^2.H^4FeCy^6 + H^2FeCy^6$. The ferrocyanide forms blue needle-shaped crystals, having a metallic lustre.

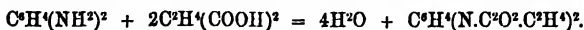
By the action of sodium nitrite on tetramethylparaphenylenediamine, *trimethylphenylenediaminenitrosamine* is obtained, and a blue colouring matter is produced, which, however, has not been isolated. The nitrosamine crystallises in greenish-yellow plates (m. p. 98°), soluble in benzene, chloroform, ether, and hot water. On reduction with tin and hydrochloric acid, it yields trimethylparaphenylenediamine, $N(CH^3)^2.C^6H^4.NH(CH^3)$, an oily liquid (b. p. 265°), sparingly soluble in water. The acetyl-derivative crystallises in hydrated prisms melting at 78° . The anhydrous crystals melt at 95° .

When an excess of sodium nitrite is added to an acid solution of tetramethylparaphenylenediamine, *nitrotrimethylparaphenylenediamine-nitrosamine*, $N(CH^3)^2.C^6H^4[N(CH^3.NO)(NO^2)]$, separates out in orange-coloured needles melting at 87° , soluble in benzene and chloroform, but insoluble in water. On reduction with tin and hydrochloric acid, this compound yields *trimethyltriamidobenzene*, $N(CH^3)^2.C^6H^4[NH(CH^3)]_3.NH^2$, which crystallises in white needles, melts at 90° , boils at 294° , and dissolves in water. Its diacetyl-derivative crystallises in white plates melting at 184° (Wurster a. Schobig, *Ber.* xii. 1807).

The formation of the red and blue colouring matters obtained by the action of oxidising agents on di- and tetramethylparaphenylenediamine respectively may be represented, according to Wurster (*Ber.* xii. 1803) by the following equations:



DISUCCINYLPARAPHENYLENEDIAMINE, $C^{14}H^{12}N^2O^4 = C^6H^4(N.C^2O^2.C^2H^4)^2$ (R. Biedermann, *Ber.* ix. 1668). This compound is obtained by heating a mixture of paraphenylenediamine and succinic acid at 200° for about half an hour:



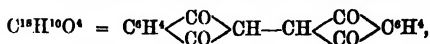
On boiling the fused mass with water, the succinyl-derivative remains as a substance slightly soluble in hot glacial acetic acid, and separating from this solution on cooling in small shining crystals. The best solvent for recrystallising it is fuming nitric acid.

Disuccinylphenylenediamine melts at a temperature above the range of the mercurial thermometer, and may be sublimed from a red-hot platinum crucible in white shining needles. It does not unite either with bases or with acids. By boiling with potash-ley, it is resolved into phenylenediamine and succinic acid. By a mixture

of strong nitric acid and strong sulphuric acid or phosphoric anhydride, it is converted into a yellow nitro-compound.

An action similar to that of succinic acid is exerted upon paraphenylenediamine by succinic anhydride and succinyl chloride. Phthalic anhydride and hydroxy-acids, salicylic acid, for example, appear also to act in like manner on para- and meta-phenylenediamine.

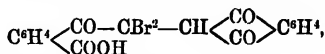
PHENYLENE-KETONIC COMPOUNDS (Gabriel a. Michael, *Ber.* x. 1559, 2199). **Ethineorthophenylenediketone** or **Ethinediphthalyl**,



is formed by heating a mixture of phthalic anhydride and succinic acid with sodium acetate, the mixture being kept in a state of fusion as long as carbon dioxide continues to escape:

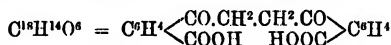


On dissolving the residue in nitrobenzene, the diketone crystallises out in yellow needles melting at a temperature above 300° . When a solution of this compound in acetic acid is heated with bromine at 100° in a sealed tube, a molecule of water is taken up, and two of the hydrogen-atoms are replaced by bromine, producing the compound:

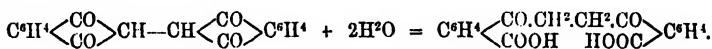


which is decomposed by fusion with alkalis.

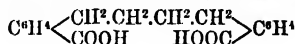
Phenylene - ethyleneketone - carboxylic, or **Ethylene - benzoylcarboxylic acid**,



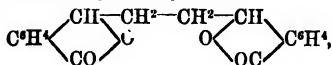
(Gabriel a. Michael, *Ber.* x. 2199). This acid is formed by the action of boiling dilute potash-ley on ethine-diphthalyl, $\text{C}^{10}\text{H}^{10}\text{O}^4$, and is precipitated from the resulting solution by hydrochloric acid:



When fused, it gives off 1 mol. water and yields an anhydride which melts at 228° – 230° . Heated to 163° in a sealed tube with hydrogen iodide and red phosphorus, it exchanges O^2 for 2H^2 , and is converted into ethylene-benzoylcarboxylic acid:



melting at 196° – 198° . Bromine converts it into dibromomethylenbenzoyl-carboxylic acid, $\text{C}^{18}\text{H}^{12}\text{Br}^2\text{O}^6$, which crystallises in long white prisms and melts at 270° – 272° . By sodium-amalgam, ethylenebenzoylcarboxylic acid is converted into the anhydride of ethylenebenzoylcarboxylic acid:



which forms long needles having a silky lustre and melting at 208° – 210° .

PHENYLENE-OKAMIC ACID, $\text{NH}^2 \cdot \text{C}^6\text{H}^4 \cdot \text{NH} \cdot \text{C}^2\text{O}^2 \cdot \text{OH}$ [1 : 3]. See OKAMIC ACIDS (p. 1457).

PHENYL-ETHER, SULPHOPHENYLIC. See THIOPHENYLIC ETHERS.

PHENYL-ETHYL ALCOHOLS AND ETHERS. *Primary Phenyl-ethyl Alcohol*, $\text{C}^6\text{H}^5 \cdot \text{CH}^2 \cdot \text{CH}^2 \cdot \text{OH}$, is formed by the action of sodium-amalgam (2 p. c. Na) on an alcoholic solution of phenylacetaldehyde, $\text{C}^6\text{H}^5 \cdot \text{CH}^2 \cdot \text{COH}$ (prepared by distilling a mixture of the calcium salts of phenylacetic and formic acids) the liquid being neutralised from time to time with sulphuric acid. It is a colourless liquid having a sp. gr. of 1.0337 at 21° , boiling without decomposition at 212° , and oxidised by chromic acid mixture to phenylacetic acid. The *acetate*, $\text{C}^6\text{H}^5 \cdot \text{CH}^2 \cdot \text{CH}^2 \cdot \text{O}(\text{C}^2\text{H}^3\text{O})$, obtained by heating the alcohol with acetic anhydride at 150° , is a colourless liquid having a strong but agreeable odour, a sp. gr. of 1.0286, and boiling without decomposition at 224° . Treated with aqueous potash and a

small quantity of alcohol, it yields potassium acetate and phenylethyl alcohol (Radziszewski, *Ber.* ix. 372).

Secondary Phenyl-ethyl Alcohol or **Acetophenonic Alcohol**, $C^6H^5.CHOH.CH^3$ (b. p. 202° – 203°), formed by the action of sodium-amalgam on a dilute alcoholic solution of phenyl-methyl ketone, has been already described (vii. 936).

Radziszewski (*Ber.* vii. 140) prepares it by dissolving the corresponding bromide (*infra*) in twice its volume of glacial acetic acid, and mixing it with twice the quantity of dry silver acetate. The mixture becomes hot, and yields—together with silver bromide and a small quantity of cinnamene—secondary phenyl-ethyl acetate, which may be dissolved out from the silver bromide by prolonged washing with glacial acetic acid. This ether, warmed with aqueous soda-ley containing a little alcohol, yields secondary phenyl-ethyl alcohol boiling constantly at 202° – 204° , and converted by oxidation into phenyl-methyl ketone.

Secondary Phenyl-ethyl Bromide or **Bromethyl-benzene**, $C^6H^5.CHBr.CH^3$ (v. 1057; vi. 292), is obtained: 1. By the action of bromine on ethylbenzene at 140° , and may be purified by washing, drying, and cooling in a freezing mixture, whereupon the styryl bromide, $C^6H^5.CHBr.CH^2Br$, formed at the same time, crystallises out (Radziszewski, *Ber.* vi. 492; comp. Berthelot, *Compt. rend.* lxvii. 328). 2. By passing hydrogen bromide into cooled secondary phenyl-ethyl alcohol, to which a small quantity of calcium chloride is added to take up water formed at the same time. The product, freed from excess of hydrobromic acid by shaking with water, is a brown-yellow liquid which fumes and gradually becomes darker on exposure to the air, and cannot be distilled without considerable decomposition (Engler a. Bethge, *Ber.* vii. 1125). The acetate, obtained from it by means of silver acetate, is converted by saponification into secondary phenyl-ethyl alcohol. The bromide, heated with an alcoholic solution of potassium cyanide, yields cinnamene, metacinnamene, and—together with other products not yet examined—a small quantity of a nitril convertible by caustic potash into a liquid acid (Radziszewski, *ibid.* 140). A mixture of phenylethyl bromide and ethylbenzene heated with zinc-dust yields the hydrocarbon $C^6H^{10} = \frac{C^6H^5}{CH^2} > CH.C^6H^4.CH^2.CH^3$, which when oxidised yields, as chief product, parabenzoylebenzoic acid, together with terephthalic, benzoic, and carbonic acids, and a ketonic compound, $C^6H^5.CO.CH^2.C^6H^4.C^2H^5$ or $C^6H^5.CH^2.CO.C^6H^{11}.C^2H^5$, which crystallises from ether in rhombic prisms melting at 120° , and smelling like fungi and bergamot oil (Radziszewski, *Ber.* vi. 494, 811; vii. 142).

PHENYLETHYLSULPHONIC ACID, $C^6H^5.SO^3H$. Cinnamene, C^6H^8 , treated with acid sodium sulphite, yields crystals consisting of the sodium salt of a phenethylsulphonic acid; but whether the acid thus produced contains primary or secondary phenyl-ethyl has not yet been ascertained (W. Miller, *N. Rep. Pharm.* xiv. 1).

PHENYL-FURFUZIDE, $C^6H^5.N^2H.C^3H^4O$. See HYDRAZINES (p. 1054).

PHENYL-GLYCERYL ALCOHOL or **PHENYL-GLYCEROL**, $C^6H^{12}O^3 = C^6H^4(C^6H^5)(OH)^3$, and **ETHERS** (Grimaux, *Bull. Soc. Chim.* [2], xx. 48). When bromine (1 mol.) dissolved in chloroform is added by drops, so as to avoid heating, to a chloroform solution of cinnyl alcohol, styryl alcohol, or styrene, $C^6H^8.OH$ (i. 992; v. 447), and the liquid is then left to evaporate, phenyl-glyceryl-dibromhydrin, styrceryl-bromhydrin, or styrene dibromide, $C^6H^2Br^2.OH$ or $C^6H^5.CHBr.CHBr.CH^2OH$, separates out as a hard crystalline mass, which, when purified by pressure and slow crystallisation from ether, forms broad white shining laminae or groups of slender needles. It melts at 74° , is insoluble in water, but dissolves readily in alcohol and ether.

Phenyl-glycerol, Phenoglycerin, or Styceerin, $C^6H^5.CHOH.CHOH.CH^2OH$, is formed, together with small quantities of other products, by boiling this dibromhydrin with water for twenty-four hours. The formation of the secondary products may be avoided by conducting the saponification in presence of silver acetate, so as to remove hydrobromic acid as fast as it is formed, then filtering, treating the filtrate with hydrogen sulphide, again filtering, concentrating the filtrate, and finally leaving it to evaporate in a vacuum. The phenyl-glycerol thus obtained is a gummy, light-yellow, bitter substance, easily soluble in water and alcohol, nearly insoluble in ether. It does not appear to alter in contact with the air, but its solution becomes brownish during evaporation. It decomposes when distilled. By distillation with formic acid, it yields carbon dioxide, water, and a thick oil (perhaps diphenyl-diallyl), boiling at about 300° .

Phenyl - glycerylacetodibromohydrin

or

Styceeryl - acetodibromohydrin,

$C^6H^5.CHBr.CHBr.CH^2(OC^2H^5O)$, obtained by heating styrceryl dibromhydrin with acetyl chloride, evaporating the product over the water-bath, and crystallising it from ether, forms oblique prisms having a pleasant odour of flowers, soluble in alcohol and ether, melting at 85° – 86° . Heated for twenty-four hours at 100° with silver acetate and glacial acetic acid, it yields, together with silver bromide, an amorphous body soluble in ether, which appears to be the corresponding triacetin.

Phenyl-glyceryl-tribromhydrin or *Styrceryl-tribromhydrin*, $C^6H^5.CHBr.CHBr.CH^2Br$, is formed on repeatedly distilling the dibromhydrin with strong hydrobromic acid, and passes over into the receiver; also on adding bromine to a solution of styryl bromide in chloroform. It crystallises in small shining needles, melts at 124° , dissolves sparingly in alcohol and ether, more readily in chloroform.

The *chlorodibromhydrin*, $C^6H^5.CHBr.CHBr.CH^2Cl$, is obtained by adding bromine to styryl chloride, $C^6H^5.CH=CH.CH^2Cl$ (v. 447), and crystallises from ether in translucent laminae, moderately soluble in chloroform, sparingly in cold ether, and melting at 96.5° .

PHENYL-GLYCOCINE, $C^6H^5.NO^2 = \begin{matrix} CH^2.NH(C^6H^5) \\ | \\ COOH \end{matrix}$. This compound, which

Michaelson a. Lippmann obtained by the action of aniline on bromacetic acid (vi. 644), is also produced from aniline chloracetate by prolonged heating with water and aniline (Schwabel, *Ber.* x. 2045), and apparently when phenylamidacetonitril, $NC.CH^2.NH(C^6H^5)$, is heated with strong potash-ley (Engler, *Ber.* vi. 1004).

Phenyl-glycoccine melts at 126° – 127° , and when heated to 140° – 150° , gives off

1 mol. water, and is converted into the indifferent compound $\begin{matrix} CH^2 \\ | \\ CO \end{matrix} > N(C^6H^5)$ (P. J.

Meyer, *Ber.* viii. 1152).

Phenyl-glycoccine dissolves recently precipitated cupric hydrate with deep green colour; the oxides of silver and mercury are not dissolved by it. With *mercuric chloride* and *stannous chloride* it forms white precipitates (Schwabel, *Ber.* x. 2045). Heated with excess of aniline, it yields needle-shaped diphenyloxethylene-carbamide, melting at 110° – 111° , together with small quantities of ethylic phenylamidoglycollate, $CH^2.NH(C^6H^5)-COOC^2H^5$, melting at 57° – 58° . Methylic phenylamidoglycollate, $CH^2.NH(C^6H^5)-COOCH^3$, formed in like manner, crystallises in needles or prisms melting at 48° (Meyer).

Phenylamidoglycollamide, $CH^2.NH(C^6H^5).CONH^2$, melting at 133° , is formed by heating monochloracetamide and aniline in molecular proportions, till the former melts. *Phenylamidoglycollanilide*, $CH^2.NH(C^6H^5).CONH(C^6H^5)$, produced in like manner from monochloracetanilide and aniline, melts at 110° – 111° ; *phenylamidoglycollotoluidide* crystallises in needles melting at 171° – 172° (Meyer).

Phenyl-glycoccine, heated with *urea* to 155° , is converted into phenyl-hydantoin (p. 1046); and the same conversion is effected by heating it to 40° in aqueous solution with potassium cyanate and ammonium sulphate (Schwabel).

PHENYL-GLYCOL, $C^6H^5.NO^2 = C^6H^5(OH)^2 = C^6H^5.CHOH.CH^2OH$. *Phenyl-ethylene Alcohol*, *Styrolene Alcohol*, *Cinnamene Alcohol*.—This diatomic alcohol is prepared from styrolene dibromide, $C^6H^5.CHBr.CH^2Br$, by means of silver nitrate or potassium acetate in acetic acid solution, or with potassium acetate or silver benzoate in alcoholic solution, and subsequent saponification of the corresponding ethers. It is very soluble in water, alcohol, ether, benzene, and glacial acetic acid, and is best purified by crystallisation from a mixture of benzene and ligroin, in which latter it is but sparingly soluble. It melts at 67° – 68° , and can be sublimed. The *diacetate*, $C^6H^5.CH(OC^2H^5O).CH^2(OC^2H^5O)$, prepared from the glycol by the action of acetic chloride or anhydride, is an oily liquid having a very faint aromatic odour; the *dibenzoate*, prepared in like manner, crystallises in slender, white, scentless needles, melting at 96° – 97° (Wachendorff a. Zincke, *Ber.* x. 1004).

PRODUCTS OF OXIDATION OF PHENYL-GLYCOL (Hunäus a. Zincke, *Ber.* x. 1486). By *chromic acid* and *potassium permanganate*, phenyl-glycol is converted into benzaldehyde, together with formic or carbonic acid; by nitric acid, on the other hand, first into benzoyl-carbinol and then into benzoyl-formic acid. With nitric acid of sp. gr. 1.35–1.38, the reaction takes place at ordinary temperatures, and on its completion, which for the preparation of benzoyl-carbinol takes place in a comparatively short time, the crude product is purified by treatment with sodium carbonate and the carbinol is extracted with ether.

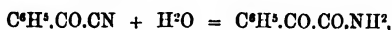
(1). *Benzoyl-carbinol*, $C^6H^5.CO.CH^2OH$, crystallises from alcohol or ether in six-sided plates, from water or dilute alcohol in shining hydrated laminae, from ligroin in prisms. The hydrated crystals melt between 73° and 74° ; the anhydrous

crystals between 85.5° and 86° ; they are partly decomposed by volatilisation, and form crystalline compounds with alkaline bisulphites. On ammoniacal silver solution and alkaline copper solution, benzoyl carbinol exerts a strong reducing action, attended with precipitation of metallic silver and cuprous oxide respectively. The *acetate*, $C^6H^5.CO.CH^2.OC^2H^3O$, prepared by the action of acetic anhydride on the alcohol, or by the action of potassium acetate and ethyl alcohol on bromacetophenone (p. 1150), crystallises from ligroin in colourless shining rhombic tablets, melting at 49° – 49.5° ; easily soluble in alcohol, ether, and chloroform. The *benzoate*, $C^6H^5.CO.CH^2.OC^2H^3O$, obtained in like manner with benzoic anhydride, crystallises from hot dilute alcohol in small tablets, melts at 117° – 117.5° , and dissolves readily in ether, chloroform, and benzene. The same benzoic ether is obtained from bromacetophenone, $C^6H^5.CO.CH^2.Br$ (p. 1150), by means of silver benzoate and toluene.

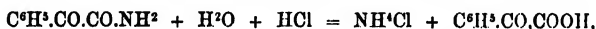
(2). *Benzoyl-formic acid*, $C^6H^5.CO.COOH$, prepared as above described, forms a *barium salt*, $(C^6H^5.CO.CO^2)^2Ba$, crystallising in prismatic laminae. The *silver salt*, $C^6H^5.CO.COOAg$, crystallises from water in small flat needles or acuminate tablets. The same acid appears to be formed by the action of nitric acid on mandelic acid, $C^6H^5.CHOH.CO^2H$.

PHENYLGLYOXALIC and PHENOXYLIC ACIDS. These are two isomeric acids obtained by the action of acids on benzoyl cyanide, and represented by the formula $C^6H^5.CO.COOH$.

Phenylglyoxalic acid, discovered by Claisen (*Ber.* x. 429, 844, 1663), is produced by treating benzoyl cyanide at ordinary temperatures with twice its weight of hydrochloric acid (sp. gr. 1.19). The cyanide then gradually dissolves, with formation of the amide of phenyl-glyoxalic acid, and afterwards sal-ammoniac and oily phenyl-glyoxalic acid separate out:



and



The latter is taken up by ether, and purified, after expulsion of the ether, by dissolving it in potassium carbonate, shaking the solution with ether (which takes up any undecomposed amide that may still be present), then acidulating and again extracting with ether, which leaves the acid as an oil, solidifying in the exsiccator to colourless prismatic crystals. After further purification through the medium of the potassium or silver salt, it melts at 65° – 66° . At a higher temperature it is resolved for the most part into benzoic acid and carbon monoxide, a smaller portion being at the same time resolved into benzoic aldehyde and carbon dioxide. It is extremely soluble in water. Its *ethylic ether*, obtained by passing hydrogen chloride into the alcoholic solution of the acid, is a fragrant liquid, insoluble in water, and boiling at 250° – 255° under ordinary pressure, at 143° – 143.5° under a pressure of 29 mm. Alcoholic potash instantly converts it into the potassium salt, $C^6H^5O^3K$, which crystallises from hot alcohol in slender, flat, concentrically grouped prisms. The silver salt, $C^6H^5O^3Ag$, obtained by precipitation, crystallises from hot water, with slight decomposition, in small plates.

The acid is reduced by sodium-amalgam to mandelic acid, $C^6H^5.CHOH.COOH$, and by hydriodic acid and phosphorus to α -toluic (phenyl-acetic) acid; these reactions establish its constitution.

Phenyl-glyoxamide, $C^6H^5.CO.CO.NH^2$. Of this compound there are three modifications. The α -amide is obtained from the above-mentioned solution by precipitation with water, as a white powder, or by agitation with ether and slow evaporation, in prismatic crystals which may be purified by recrystallisation from carbon sulphide. It then melts at 90° – 91° , dissolves easily in ether, alcohol, benzene, and chloroform, slowly in water, and has a sharp and slightly bitter taste. It dissolves easily in dilute alkalis, and carbon dioxide throws down from the solution a crystalline precipitate consisting of the β -amide, which melts at 64° – 65° , and dissolves sparingly in cold water, scarcely at all in ether, easily in alcohol. The γ -amide is precipitated on dropping the α -amide into excess of dilute hydrochloric acid, as a white powder, melting at 130° , nearly insoluble in ether, benzene, and chloroform; easily soluble in alcohol, and crystallising from the latter in tufts of slender prisms, from hot water in small four-sided plates. On passing carbon dioxide into its alkaline solution, the β -amide is produced. The β - and γ -amides dissolve in strong sulphuric acid with deep yellow colour. All the three amides, when heated with alkalis as long as ammonia is thereby evolved, and then acidulated, are reconverted into the original phenyl-glyoxalic acid.

Phenoxylic acid, discovered by Hübner a. Buchka (*Ber.* x. 479), is obtained

by heating benzoyl cyanide to 140° in sealed tubes with glacial acetic acid saturated with dry hydrogen chloride. The first product of the reaction is the compound $(C^6H^5.CO.CN.H)^2O$, which separates, on diluting the contents of the tube, as a yellow-brown powder, and may be crystallised from alcohol or acetic acid. By boiling with water, or more quickly with alkalis or acids, it is converted into phenoxylic acid, which melts at 111° , forms a *barium salt*, $(C^6H^5.CO.COO)^2Ba$, crystallising in tablets, and with lead acetate, small white needles of the *lead salt*, $(C^6H^5.CO.COO)^2Pb + 2H^2O$, which gives off its water at 200° .

PHENYL-HYDANTOÏN, $C^6H^5.NO^3$. See HYDANTOÏN (p. 1046).

PHENYL-HYDRAZINE, $C^6H^5.NH.NH^2$. See HYDRAZINES (pp. 1048–1057).

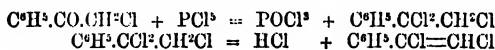
PHENYLIMIDOCHLORACETIC ETHER, $C^6H^5.N=CCl-COOC^6H^5$. See OXAMIC ETHERS (p. 1457).

PHENYLISOBUTANE, $C^6H^5.CH^2.CH(CH^3)^2$, is formed by the action of sodium on benzyl chloride and isopropyl iodide mixed with ether (Köhler a. Aronheim, *Ber.* viii. 508).

PHENYL-KETONES. See pp. 1149–1156. On *Phenylchloromethyl ketone* or *Chloracetophenone*, $C^6H^5.CO.CH^2Cl$, the following observations have been made by Dyckerhoff (*Ber.* ix. 1216; x. 119, 531). By treatment with potassium thiocyanate, the ketone is converted into phenyl-thiocyanomethyl ketone or thiocyanacetophenone, $C^6H^5.CO.CH^2SCN$, which separates in fine crystals melting at 72° – 73° . Crystalline compounds are also formed by treating chloracetophenone with cyanide or cyanate of potassium.

Thiocyanacetophenone, boiled with tin and hydrochloric acid, is converted, with simultaneous emission of a strong odour of mercaptan, into an isomeric compound which forms slender needles sparingly soluble in all solvents, and melting at 203° – 204° . The same body is formed by boiling the thiocyno-compound with hydrochloric acid. It dissolves in alkalis, and is reprecipitated by acids. The thiocyno-derivative is quickly oxidised by dilute nitric acid to carbonic, benzoic, and sulphuric acids.

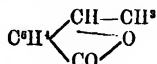
Chloracetophenone is converted by *phosphorus pentachloride*, with separation of hydrochloric acid, into α - β -dichlorostyrolene, $C^6H^5.CCl=CHCl$, according to the equation:



If an excess of chlorine be used in the preparation of chloracetophenone, the chief product obtained is the dichloride, $C^6H^5OCl^2 = C^6H^5.CO.CHCl^2$, which boils between 250° and 255° . If the passage of the chlorine be further continued, a thick black greasy mass is obtained, yielding by distillation nothing but benzoyl chloride and less chlorinated products of higher boiling point (Dyckerhoff).

Acetophenone-ortho-carboxylic Acid, $C^6H^5O^3 = C^6H^4 \begin{smallmatrix} \diagup CO.CH^3 \\ \diagdown COOH \end{smallmatrix}$ (Michael a. Gabriel, *Ber.* x. 1555, 2199; xi. 1007). This acid is formed from benzoyl-aceto-(ortho-) carboxylic acid, $C^{10}H^8O^3$, by boiling the latter in aqueous or alkaline solution, or by keeping it for some time in a state of fusion: $C^{10}H^8O^3 = C^6H^5O^3 + CO^2$; also by heating phthalylacetic acid (*q.v.*) with water at 200° : $C^{10}H^8O^3 + H^2O = C^6H^5O^3 + CO^2$. It forms crystals having a vitreous lustre, a sweet taste, and melting at 114° . Its salts show but little tendency to crystallise.

When acetophenonecarboxylic acid is treated with *sodium-alloy* ($1\frac{1}{2}$ p. c. Na), and the resulting solution is treated with hydrochloric acid, an oil is precipitated which distils over with vapour of water, and may be separated by agitation with ether. This oil solidifies below 0° , and melts at the heat of the hand. Its composition is represented by the formula

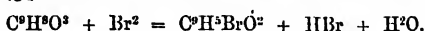


It is not dissolved by ammonia or by cold potash or soda-ley; it dissolves, however, in baryta-water, and silver nitrate added to the solution throws down slender crystals of the salt, $C^6H^4 \begin{smallmatrix} \diagup CH(OH)CH^3 \\ \diagdown \quad \quad COOAg \end{smallmatrix}$. Stronger reducing agents, such as red phosphorus and hydriodic acid, convert acetophenonecarboxylic acid into ethylbenzoic acid, $C^6H^4 \begin{smallmatrix} \diagup C^2H^5 \\ \diagdown \quad \quad COOH \end{smallmatrix}$ (Michael a. Gabriel).

Tribromacetophenone-o-carboxylic acid, $CBr^3.CO.C^6H^4.COOH$, formed by the action of bromine on a solution of phthalylacetic acid in dilute acetic acid, melts at 159° –

160°, and is resolved by alkalis into phthalic acid and bromoform. The corresponding chlorinated acid melts at 144°.

When, on the other hand, a mixture of bromine, glacial acetic acid, and acetophenone-carboxylic acid is heated in sealed tubes, bromomethylene-phthalyl, $C^6H^5BrO^2 = C^6H^5 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CHBr$, is formed, according to the equation,



The contents of the tubes are heated on a water-bath to expel hydrobromic and acetic acids, and the residue is dissolved in hot alcohol. On evaporating the alcoholic solution, bromomethylenephthalyl crystallises out, and after diluting the mother-liquor with water, an oily liquid separates, which on boiling with water deposits a yellow crystalline mass which has the composition $C^6H^5O^3$, melts at 145°–146°, and begins to sublime at 100°. Bromomethylenephthalyl dissolves easily in benzene, chloroform, carbon bisulphide, glacial acetic acid, and hot alcohol, and crystallises in long flexible needles melting at 132°–133°.

PHENYL-LACTIC ACID, $C^6H^{10}O^3 = C^6H^5.CH^2.CH(OH).COOH$. On the formation of this acid by the action of water on hydrobromocinnamic acid, see p. 500.

PHENYL-METHANES. On DIPHENYL-METHANE, $CH^2(C^6H^5)^2$, see vii. 947; viii. 682. On TRIPHENYL-METHANE, vii. 948.

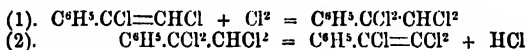
PHENYL-METHYL-OXAMIDE, $NH(CH^3).CO.NH(C^6H^5)$. See OXAMIDE (p. 1458).

PHENYL-OXAMETHANE, $C^6H^5.CO.NH.COOC^2H^5$. See OXAMIC ETHERS (p. 1457).

PHENYL-OXAZIDE. Syn. with OXALYL - DIPHENYLHYDRAZIDE, $(C^6H^5.N^2H^2)^2C^2O^2$. See HYDRAZINES (p. 1053).

PHENYL-OXYCROTONIC ACID. Syn. with CINNAMOMANDRIC ACID, $C^{10}H^{10}O^3 = C^6H^5.CH=CH.CH(OH).COOH$ (p. 507).

PHENYL-PERCHLORETHYLENE, $C^6H^5Cl^3$, is formed, with evolution of hydrogen chloride, by distilling tetrachlorocinnamene, which latter is produced by the action of chlorine at ordinary temperatures on α - β -dichlorocinnamene:



(Dyckerhoff, *Ber.* x. 531).

PHENYL-PHOSPHINES. See PHOSPHINES.

PHENYL-PROPIONIC ACID, $C^6H^{10}O^2 = CH^2(C^6H^5).CH^2.COOH$. *Hydrocinnamic acid* (vi. 468).—This acid is formed by oxidising phenyl-propyl alcohol dissolved in glacial acetic acid with somewhat less than the theoretical quantity of chromic acid. Its *calcium salt*, $(C^6H^5O^2)^2Ca + 1\frac{1}{2}H^2O$, crystallises in stellate groups of needles. The *benzyl ether*, $C^6H^5O^2.CH^2.C^6H^5$, formed by the action of sodium on benzyl acetate, has been already described (p. 1068). The *phenyl-propylic ether*, $C^6H^5O^2.C^6H^5(C^6H^5)$, obtained by the action of sodium-amalgam and water on styraeyl tetrabromide, is a colourless mobile oil (W. v. Miller, *Ber.* ix. 274).

Phenyl-bromopropionic acid, $C^6H^5BrO^2$, and the corresponding *iodine-derivative*, discovered by Glaser (vi. 417), are respectively identical with hydrobromo- and hydriodo-cinnamic acid, but, according to F. Binder (*Ber.* x. 518), their reactions do not quite agree with those described by Glaser. The brominated acid is resolved at 143° into hydrobromic and cinnamic acids, and at 150° in a stream of air, the decomposition is complete. The same change takes place on boiling the brominated acid with water, but the greater part of it is converted into phenyl-lactic or phenyl-hydroxypropionic acid, $C^6H^5(OH)O^2$, which may be advantageously prepared by this reaction. Phenyl-iodopropionic acid reacts with water in a similar manner, the greater part of it being, however, resolved into hydriodic and cinnamic acids.

Phenyl-bromopropionic acid, treated with excess of dilute soda-ley, is immediately decomposed, with separation of cinnamene, small quantities of cinnamic and phenyl-lactic acids being formed at the same time. Phenyl-iodopropionic acid is decomposed in the same manner, excepting that it yields a larger proportion of cinnamene (70 per cent. of the theoretical amount). Now, as phenyl-lactic acid has the constitution $C^6H^5.CH^2.CH(OH).COOH$, and consequently phenyl-bromopropionic acid must be $C^6H^5.CH^2.CHBr.COOH$, the above-mentioned formation of cinnamene shows that this hydrocarbon is an unsaturated compound represented by the formula $C^6H^5.CH^2.CH$ (Binder).

Phenyl-propionitril, $C^6H^5.CH^2.CH^2.CN$, is the principal constituent of the volatile oil of water-cress (Hofmann, p. 584).

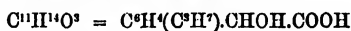
PHENYL-PROPYL ALCOHOL, $C^9H^{12}O = C^6H^5.CH^2.CH^2.CH^2OH$ (Rügheimer, *Ber.* vi. 214). This alcohol is obtained, together with a small quantity of allyl-benzene, C^9H^{10} , by treating a warm aqueous solution of styryl alcohol, $C^9H^{10}O$, with sodium-amalgam in a reflux apparatus heated in the water-bath, agitating with ether, and submitting the product to fractional distillation. It is a viscid, colourless, strongly refracting liquid, having a density of 1.008 at 18°, boiling at 255° (uncorr.), and not solidifying at -18° . It is only slightly soluble in water, but mixes in almost all proportions with alcohol, ether, and glacial acetic acid. When dissolved in a small quantity of the latter and oxidised with somewhat less than the calculated quantity of chromic acid, it is converted into phenyl-propionic acid.

Phenyl-propyl Acetate, $C^9H^{11}.O.C^2H^3O$, is formed, with violent reaction, on mixing the alcohol with acetyl chloride. It is a slightly yellow, nearly scentless liquid, much more mobile than the alcohol, boiling at 244°–245°, not solidifying at -18° . The *benzoate*, prepared by heating the alcohol with benzoyl chloride, is a thick brownish liquid. The *phenyl-propionate*, $C^9H^{11}.C^7H^5O^2$, has been already described.

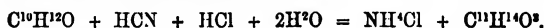
Phenyl-propyl Bromide, $C^9H^{11}Br = C^6H^5.CH^2.CH^2.CH^2Br$, formed by passing bromine-vapour into normal propyl-benzene heated to 150°–160°, is resolved by boiling into hydrogen bromide and allyl-benzene, $C^6H^5(C^3H^3)$ (Radziszewski, *Compt. rend.* lxxviii. 1163).

Phenyl-propyl Ketones. See KETONES (p. 1152).

PHENYL-PROPYLGLYCOLLIC ACID,



(A. Raab, *Ber.* viii. 592). This acid, homologous with mandelic acid (p. 1261), is prepared by heating an alcoholic solution of cumic aldehyde to 120°–130° for fifteen hours with hydrocyanic and hydrochloric acids:

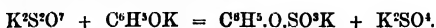


The yield, however, is very small. The acid crystallises in small white needles, which melt at 158°, dissolve with moderate facility in water, very readily in alcohol and ether. The *barium salt*, $(C^{11}H^{13}O^3)^2Ba + 4H^2O$, is moderately soluble in boiling water, and crystallises therefrom in small rhombic plates. The *silver salt*, $C^{11}H^{13}O^3Ag$, separates from a mixture of the barium salt with silver nitrate in stellate groups of slender needles. The *lead salt*, $(C^{11}H^{13}O^3)^2Pb$, is a white nearly insoluble precipitate.

PHENYL-SEMICARBAZIDE, $C^6H^5.N^2H^2.CO.NH^2$. See HYDRAZINES (p. 1055).

PHENYL-SULPHACETIC, -SULPHINACETIC, and -SULPHON-ACETIC ACIDS. See SULPHALKYLACETIC ACIDS.

PHENYL-SULPHURIC ACID, $C^6H^5.O.SO^2H$. The potassium salt of this acid may be formed synthetically by heating a concentrated aqueous solution of potassium phenate with potassium pyrosulphate:



This salt is slightly soluble in cold, moderately soluble in hot alcohol, easily in water. When quickly heated to fusion and then dissolved in water, it gives a ruby-red colour with ferric chloride. It is decomposed by dilute hydrochloric acid, yielding phenol and sulphuric acid (E. Baumann, *Ber.* ix. 1715).

Potassium phenyl-sulphate is found in the urine after the introduction of phenol into the organism, being formed by the action of the phenol on potassium sulphate present therein. Phenyl-sulphates occur also in the urine of the horse and other mammalia, their formation being especially promoted by vegetable diet (Baumann, *Pflüger's Archiv. f. Physiologie*, xii. 69; xiii. 285; *Ber.* ix. 54; *Chem. Soc. J.* xxix. 726; xxx. 109, 212, 534).

On *Methyl-phenylsulphuric* or *Cresylsulphuric acid*, $C^6H^4(CH^3).O.SO^2H$, see p. 584.

PHENYL-THIOCARBAMIDE, $NH^2.CS.NH(C^6H^5)$ See CARBAMIDES (THIO-), (p. 396).

PHENYL-THIOCARBAZIDE. See HYDRAZINES (pp. 1055, 1056).

PHENYL-THIOCARBIMIDE, $CS=N-C^6H^5$. On the reaction of this compound with aldehyde-ammonia, see p. 399.

PHENYL-TOLUENE, $C^6H^1(C^6H^3)$. On the decomposition of this hydrocarbon by Heat, see Barbier (p. 1065).

PHENYL- (DI-) TOLYL-CARBAMIDE, $N(C^6H^3)_2.CO.N(C^6H^1.CH^3)$. See CARBAMIDES (p. 391).

PHENYL-URETHANE, $NH^2.CO.OC^6H^5$. See CARBAMATES (p. 382).

PHENYL-VALERIC ACID, $C^6H^5(C^6H^3)O^2$. The benzylic ether of an acid having this composition is obtained by the action of sodium on benzyl butyrate. This ether boils at 240° – 250° ; the acid obtained from it melts at 78° (Conrad a. Hodgkinson, *Ber.* x. 254).

PHENYL-XYLENE, $C^{14}H^{14} = C^6H^1(CH^3).CH^2.C^6H^5$, is formed by heating xylyl chloride, $C^6H^1(CH^3).CH^2Cl$ (b. p. 192° – 196° , from coal-tar xylene), with 3 vol. benzene and zinc-dust. When purified by fractional distillation and rectification over sodium, it is a liquid boiling at 283° – 286° (corr.), having a density of 1.01 at 0° , a blue fluorescence, and a faint alliaceous odour. At a red heat it is quickly resolved into anthracene, xylene, benzene, and hydrogen (Barbier, *Compt. rend.* lxxix. 660; *Ann. Chim. Phys.* [5], vii. 515).

PHILLIPIUM. See YTTRIUM-METALS.

PHILLIPSITE. This mineral occurs, together with other zeolites, in the cavities of the basalt of the Limperichkopf, near Asbach, and of Geisnidda, Vogelsberg. In the former locality it is the oldest of the zeolites, being followed in order by natrolite and apophyllite; in the latter it follows gismondin, and is itself succeeded by chabasite (Weiss, *Jahrb. f. Min.* 1873, 319; Sandberger, *ibid.* 1874, 173). At Stempel, near Marburg, phillipsite occurs, together with natrolite and analcime, the natrolite being the oldest of the three zeolites, and the analcime the most recent (A. v. Koener, *ibid.* 75. 116). The occurrence of phillipsite, and other zeolites of recent formation, near Oran, in Algeria, has been observed by Daubrée (*Compt. rend.* lxxiv. 157; *Chem. Soc. J.* xxxi. 444).

According to A. Streng (*ibid.* 585), phillipsite, hitherto regarded as orthorhombic (iii. 13), belongs, as also does baryta-harmotome, to the monoclinic system; and this view is confirmed by the crystallographical and optical measurements of Trippke (*Jahrb. f. Min.* 1879, 681; *Chem. Soc. J.* xxxvi. 515).

Phillipsite from Richmond, Victoria, analysed by C. Newbery (*Jahrb. f. Min.* 1871, 75), was found to contain:

SiO^2	Al^2O^3	CaO	K^2O	Na^2O	H^2O
46.62	23.60	4.48	6.39	5.10	14.76 = 100.95

PHLOBAPHENE. This name is applied to certain red bodies, formed, together with glucose, when many tannins are heated with dilute sulphuric acid. By fusion with potash, they are resolved into protocatechuic acid, and another body, which is either a fatty acid, or phloroglucol, according to the kind of tannin employed (H. B. Procter, *Chem. News*, xxxix. 245; *Chem. Soc. J.* xxxvi. 979). According to C. Etti (*Dingl. pol. J.* cccxviii. 351) the dark-red substance which remains on evaporating the yellowish alcoholic solution of lupulo-tannin from hops, has the composition $C^{25}H^{40}O^{23}$, and may be supposed to result from the expulsion of one molecule of water from 2 mols. of a tannic acid of the formula $C^{25}H^{24}O^{13}$. To obtain it, coarsely powdered hop flowers are placed in an extraction apparatus, and the mass, after being freed from resin and bitter principle as much as possible, is extracted with 20 per cent. alcohol. On evaporating to a small bulk and cooling, a red precipitate of lupulo-phlobaphene is formed; this is dissolved in 90 per cent. alcohol, evaporated to dryness, and heated at 120° – 130° . If it tastes bitter, the bitter-principle may be removed by ether. Lupulo-phlobaphene is easily soluble in alkalis, and is precipitated unchanged by dilute mineral acids. On boiling the freshly precipitated and not previously heated phlobaphene with dilute mineral acids, it is decomposed, glucose and 1 mol. of water being split off.

As the phlobaphene is easily prepared, is constant in composition, and precipitates gelatin solution completely, it may be estimated quantitatively like tannin, and used for standardising the solution employed.

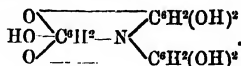
PHLOGOPITE. See MICA (p. 1321).

PHLOREIN, $C^{18}H^{11}NO^7$ (R. Benedikt, *Ber.* vii. 445; *Liebig's Annalen*, clxxviii. 92). A colouring matter produced by the action of nitrous acid on phloroglucol. It is a dark green powder having a metallic lustre, insoluble in water, but dissolving easily in alcohol, ether, and acetic acid with dark brown colour, in alkalis and alkaline carbonates with deep purple colour. Benedikt deduced, from his first analyses of this body, the formula $C^{18}H^8O^8$, and represented its formation by the equation

$2\text{C}^6\text{H}^6\text{O}^3 = \text{C}^{12}\text{H}^6\text{O}^3 + \text{H}^2\text{O} + \text{H}^2$; but from subsequent analyses he infers that it contains nitrogen, and has the composition $\text{C}^{16}\text{H}^{11}\text{NO}^7$, according to which its formation may be represented by the equation:



For its constitution he proposes the formula



PHLORETIC ACID, $\text{C}^{16}\text{H}^{10}\text{O}^5$. H. Schiff (*Liebig's Annalen*, clxxii. 356) prepares phloretic acid, together with phloroglucol, by boiling phloretin in portions of 20 grams for about three hours in a reflux apparatus, with 150 c.c. of potash-ley of sp. gr. 1.20; saturates the liquid when cold with sulphuric acid; then adds sodium bicarbonate in very slight excess, and extracts the phloroglucol by repeated agitation with an equal volume of ether; a larger excess of the bicarbonate interferes with the complete extraction of the phloroglucol. The remaining alkaline liquid is finally supersaturated with sulphuric acid, and the phloretic acid extracted by agitation with ether four times repeated. The phloroglucol thus obtained is quite pure; the phloretic acid still retains a small quantity of phloroglucol (compare Hlasiwetz, iv. 489).

Phloretic acid treated with *phosphorus oxychloride* at about 60° dissolves, with evolution of hydrochloric acid; and after about an hour the whole solidifies to a white mass; and on washing this mass with ether, alcohol, and water, and dissolving it at boiling heat in glacial acetic acid, a solution is obtained which on cooling deposits white crystals of triphloretid, $\text{C}^{24}\text{H}^{20}\text{O}^7 = 3\text{C}^6\text{H}^{10}\text{O}^3 - 2\text{H}^2\text{O}$. This compound does not give the reactions of tannic acid (Schiff, *Ber.* vi. 759).

Methyl-phloretic acid, $\text{C}^{16}\text{H}^{12}\text{O}^3 = \text{C}^6\text{H}^4(\text{CH}_3)^2\text{O}^3$, is prepared by mixing the solutions of 1 mol. phloretic acid and $2\frac{1}{2}$ mols. potassium hydrate in methylic alcohol, and slowly evaporating to dryness. The product is then mixed with a quantity of dry methyl alcohol sufficient to form a thin paste, and methyl iodide (8 mols.) is gradually added, whereby a crystalline mass is obtained, consisting of potassium iodide and *methylic methylphloretate*, with some potassium methylphloretate. The methylic methylphloretate, which may be separated by dissolving the mass in water, and agitating with ether, crystallises in lustrous tables, which have a pleasant odour, resembling that of methyl anisate. It melts at 38° , and boils at 278° . This ether is easily decomposed by an aqueous solution of potassium hydrate, and the addition of hydrochloric acid then separates the methylphloretic acid in the crystalline state. The acid is only slightly soluble in cold water, more readily when heated, and very soluble in alcohol and ether. It crystallises in prisms, which sublime below 100° , and melt at 103.4° . The barium salt crystallises readily in thin plates; the potassium salt in tufts of needles.

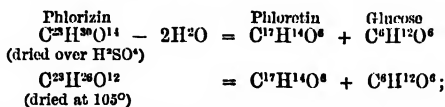
Ethyl-phloretic acid, prepared in a similar manner with ethyl alcohol and ethyl iodide, crystallises in white lustrous scales melting at 106.5° ; in other respects it closely resembles the methyl derivative.

When methylphloretic acid is added to a cold mixture of potassium dichromate, sulphuric acid and water, a violent action takes place, resulting in the formation of methylparaoxybenzoic (anisic) acid; if the reaction be moderated, the corresponding aldehyde is obtained. Ethylphloretic acid similarly treated yields paraethoxybenzoic acid, $\text{C}^6\text{H}_4\text{OC}^2\text{H}^3\text{H}^2\text{CO}^2\text{H}^2$, melting at 195° (vi. 899). From these results it follows that phloretic acid has only one side-chain containing carbon, and must therefore have the constitution of phenoxypropionic acid, $\text{C}^6\text{H}^4(\text{OH})\text{CH}^2\text{CH}^2\text{COOH}$, or of phenoxyisopropionic acid, $\text{C}^6\text{H}^4(\text{OH})\text{CH} \begin{smallmatrix} \text{CH}^3 \\ \diagup \\ \text{COOH} \end{smallmatrix}$, the hydroxyl being in the para-position with respect to that side chain (Körner a. Corbetta, *Ber.* vii. 1731).

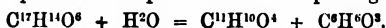
PHLORETIN, $\text{C}^{18}\text{H}^{14}\text{O}^5$. H. Schiff (*Liebig's Annalen*, clxxii. 356) prepares this compound by dissolving phlorizin (20 g.) in water (140 g.) heated nearly to boiling, adding 50 g. of 20 per cent. sulphuric acid previously heated nearly to boiling, and keeping the mixture nearly at the boiling heat. After a few minutes the liquid solidifies to a pulp of perfectly white crystals of phloretin.

PHLORIZIN. The formula $\text{C}^{21}\text{H}^{24}\text{O}^{10}$, usually assigned to this body, is founded on the analysis of Stas, which gives 57.47 per cent. carbon and 5.67 hydrogen, the calculated quantities being 57.79 C. and 5.51 H. (see Gmelin's Handbook, English Edition, xvi. 13). According to this formula, and those of phloretin and phloretic acid above given, the resolution of phlorizin into glucose and phloretin is represented

by the equation $C^{21}H^{24}O^{16} + H^2O = C^6H^{12}O^4 + C^{15}H^{14}O^3$; and that of phloretin into phloretic acid and phloroglucol under the influence of alkalis, by the equation $C^{17}H^{14}O^3 + H^2O = C^6H^{10}O^3 + C^6H^6O^3$ (iv. 489, 494). According to J. Löwe, on the other hand (*Zeitschr. anal. chem.* 1876, 28), the formula of phlorizin dried over sulphuric acid is $C^{23}H^{30}O^{14}$; of phlorizin dried at 100° – 105° , $C^{23}H^{28}O^{12}$; of phloretin, $C^{17}H^{14}O^3$; and of phloretic acid, $C^{11}H^{10}O^4$. Löwe finds also that phlorizin is not precipitated either by lead salts or by barium salts, and that it is resolved into phloretin and glucose when heated to 110° even in pure water, and when heated to 130° in the dry state. These decompositions he represents by the following equations:



and the resolution of phloretin into phloretic acid and phloroglucol by the equation:

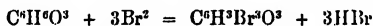


It must be observed, however, that the percentages of carbon required by Löwe's formulæ of phlorizin, phloretin, and phloretic acid are lower than those found by all other chemists who have examined these bodies (see Gmelin's Handbook, xiii. 308; xv. 8, 11), and that the formula $C^6H^{10}O^3$ for phloretic acid is supported by the composition of methyl- and ethyl-phloretic acids (p. 1569). Moreover, it is not easy to see how Löwe's formula for phloretic acid can be reconciled with the formation of anisic acid by oxidation of methyl-phloretic acid.

Phlorizin gives a dark blue colour with ammonium sulphomolybdate (p. 1335).

A solution of 0.046 grm. phlorizin in 100 c.c. alcohol, or of 0.039 grm. in 100 c.c. wood-spirit, has a specific rotatory power of +52 for the yellow ray (*Oudemans, Pogg. Ann.* cxlviii. 337).

PHLOROBROMIN, C^6HBr^2O (*Benedikt, Liebig's Annalen*, clxxxix. 165). When bromine (10 pts.) is gradually added to an aqueous solution of phloroglucol (1 pt.), tribromophloroglucol is first formed, and subsequently converted into phlorobromin:



and



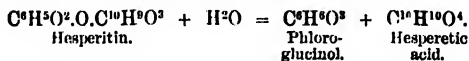
To obtain the latter compound pure, the liquid is decanted from the hard lumps formed in the reaction; these are left to dry in the air and crystallised from chloroform; the prisms thus obtained are heated on the water-bath with water and excess of bromine till the bromine is driven off; and the residue is recrystallised from chloroform.

Phlorobromin thus obtained crystallises in colourless orthorhombic prisms, $OP \cdot \infty P \cdot \infty \bar{P}$, having the axial ratio $a : b = 1 : 1.988$, and the angles $\infty \bar{P} \infty : \infty P = 39^\circ 55'$; $\infty P : \infty \bar{P} = 79^\circ 50'$ and $100^\circ 10'$. The crystals melt at 152° ; decompose at a higher temperature, are insoluble in water, and are not attacked either by boiling potash-ley, boiling nitric acid, or sodium-amalgam.

When phlorobromin is dissolved in warm alcohol, and the solution, after standing for some hours, is mixed with a large quantity of cold water, an oil is precipitated together with slender needles of pentabromactone melting at 76° (vi. 27).

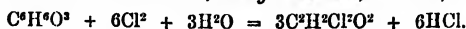
Phlorobromin is decomposed by aqueous ammonia at ordinary temperatures, yielding, together with bromoform, a body having the composition $C^6Br^4H^4N^2$, which may be purified by precipitation from the ammoniacal solution with excess of sulphuric acid, extraction with ether, evaporation of the ethereal solution, and recrystallisation of the residue from water with the aid of blood-charcoal. It then forms large white crystals or transparent laminae melting at 124° . It is decomposed by potash, with formation of ammonia and bromoform, and converted into a brominated acid by heating to 120° for several hours with dilute sulphuric acid.

PHLOROGLUCOL, $C^6H^6O^3 = C^6H^4(OH)^2$. *Phloroglucin*.—This triatomic alcohol is formed: 1. Together with another substance, by fusing resorcinol ($C^6H^4O^2$) with sodium hydrate, the phloroglucin constituting from 60–70 per cent. of the product (*Barth u. Schreder, Ber.* xii. 503). 2. Together with small quantities of other products, by fusing resorcinoldisulphonic acid with potassium hydrate; soda yields a less favourable result (*Tedeschi, Ber.* xii. 1267). 3. Together with hesperetic acid, by heating hesperitin to 100° with potash (*E. Hoffmann, Ber.* ix. 685):



Reactions.—1. When a solution of *potassium nitrite* is added to a very dilute solution of phloroglucol mixed with *nitrate of toluidine* (or *aniline*), the liquid, which is at first clear, becomes brownish-yellow, then orange-red, and ultimately deposits a cinnabar-red precipitate. This is a very delicate test for phloroglucol. A similar reaction is however produced by maclurin, catechin, decoction of fustic, and extract of hops (Weselsky, *Ber.* ix. 216): See also Procter (*Chem. News*, xxxix. 245; *Chem. Soc. J.* xxxvi. 979).

2. By the action of *chlorine* and *water*, phloroglucol is converted into dichloro-acetic acid (Hlasiwetz a. Hubermann, *Liebig's Annalen*, clv. 120):



3. With *bromine* and *water*, it yields tribromophloroglucol, afterwards converted into phlorobromin, $\text{C}^6\text{HBr}^4\text{O}$.

4. With nitrous acid it yields phloroin, $\text{C}^{12}\text{H}^8\text{O}$ (p. 1568).

Trinitrosophloroglucol, $\text{C}^6(\text{NO})^3(\text{OH})^3$ (Benedikt, *Ber.* xi. 1374). When a concentrated well-cooled solution of potassium nitrite is added to a solution of phloroglucol in dilute acetic acid covered with a layer of ether, the mixture becomes dark-brown, and after some minutes an acid potassium salt begins to separate. On supersaturating the solution with potash, and adding alcohol, the neutral potassium salt is thrown down in beautiful green needles amounting to about 70 per cent. of the theoretical yield. As this *potassium trinitroso-phloroglucol*, $\text{C}^6(\text{NO})^3(\text{OK})^3$, cannot be recrystallised without great loss, it must be dissolved in water and precipitated with alcohol, to which some potash has been added. It is easily soluble in water, with difficulty in dilute potash, quite insoluble in weak alcohol. It may be heated to above 130° without decomposition, but explodes at a high temperature. A drop of sulphuric or nitric acid will also occasion violent explosion. A lead salt of trinitroso-phloroglucol is obtained by precipitating a dilute solution of the potassium salt with lead acetate, and falls as a yellow precipitate. When dried it forms a light cinnamon-brown powder, exploding with violence when heated. Nitroso-phloroglucol can be isolated by cautious decomposition of this lead salt mixed with alcohol, by means of sulphuric acid. On filtering and evaporating the alcoholic solution, groups of needles are obtained, which are easily soluble in water and alcohol, insoluble in ether.

The number of nitrosyl-groups that can be introduced into a phenol is—so far as can be judged from the small number of examples at present known—equal to the number of hydroxyl-groups contained therein. The introduction of the NO-group into the hydrocarbons (benzene and naphthalene) is difficult and can be effected only by indirect means, whereas the monhydric phenols, phenol, thyniol, and naphthol, take up one NO-group with ease; the dihydric phenols, resorcinol, and orcinol, give dinitroso-derivatives; and the trihydric phenol, phloroglucol, yields trinitroso-phloroglucol.

Trinitro-phloroglucol, $\text{C}^6(\text{NO}_2)^3(\text{OH})^3 + \text{H}_2\text{O}$ (Benedikt, *loc. cit.*) On adding powdered potassium nitroso-phloroglucol in very small quantities at a time to a mixture of nitric acid and sulphuric acid, oxidation takes place at the ordinary temperature, and finally yellow needles of trinitro-phloroglucol separate out. The mass is then diluted with water, exhausted with ether, and the product recrystallised from boiling water. It crystallises in hexagonal prisms modified by combination with the pyramid and prism of the second order, the combination being represented by the formula $\infty \text{P} \cdot \text{P} \cdot \infty \text{P}^2$.

Trinitro-phloroglucol loses its crystallisation-water at 100° . At 130° it begins to sublime; at 158° it melts without decomposition, but explodes on further heating. It is easily soluble in hot water, alcohol, and ether, and is decomposed by sulphuric acid only at a high temperature. Like picric acid, it possesses great tinctorial power for animal matters, the tint, however, being richer and more beautiful. It gives the isopurpuric acid reaction with potassium cyanide. On reduction with hydrogen sulphide or tin and hydrochloric acid, it appears to form the compound analogous to picramic acid. On boiling the tin solution it becomes decolorised, but does not appear to yield the corresponding triamido-compound.

Salts of Trinitro-phloroglucol.—This body decomposes carbonates readily, and forms with metals three series of salts containing 1, 2, and 3 equivalents of metal. All are explosive. The *potassium salts* are formed by saturating 2 mols. of the nitro-compound with 1, 2, or 3 mols. of potassium carbonate, working with a solution as concentrated as possible. The compound $\text{C}^6(\text{NO}_2)^3(\text{OK})^3$ forms orange-red shining needles often an inch long, whilst $\text{C}^6(\text{NO}_2)^3(\text{OK})^2\text{OH}$ is of a deep-yellow colour, and not so shining as the preceding. The compound $\text{C}^6(\text{NO}_2)^3(\text{OK})(\text{OH})^2 + \text{H}_2\text{O}$ forms long, silky, sulphur-yellow needles, losing water at 100° , and becoming dull. All three potassium-derivatives are sparingly soluble in cold water. The *neutral ammonium derivative* behaves like the corresponding potassium compound. The *barium compound*

formed by adding baryta-water to an aqueous solution of trinitro-phloroglucol, consists of microscopically small, sulphur-yellow needles, insoluble in cold or boiling water.

Lead acetate gives, in an aqueous solution of the acid, an amorphous, flocculent precipitate of *plumbic trinitro-phloroglucol*.

Phloroglucide Anhydride, or **Phloroglucide**, $\text{C}^{12}\text{H}^{10}\text{O}^5 = \text{C}^6\text{H}^3(\text{OH})^2 \cdot \text{O} \cdot \text{C}^6\text{H}^3(\text{OH})^2$, is obtained: 1. By the action of heat on phloroglucol, $2\text{C}^6\text{H}^3\text{O}^3 - \text{H}^2\text{O} = \text{C}^{12}\text{H}^{10}\text{O}^5$ (Piccard, *Ber.* vii. 891). 2. By heating phloroglucol with concentrated aqueous hydriodic or hydrochloric acid (Hlasiwetz, vi. 928). 3. By heating phloroglucol for several hours with phosphorus oxychloride. On distilling off the excess of the latter, treating the residue first with water, then with alcohol, and finally washing it with ether as long as the ether is thereby coloured red, the phloroglucide is obtained in scales unctuous to the touch (H. Schiff, *Liebig's Annalen*, clxxii. 358). It dissolves in hot water, and separates therefrom as a white tasteless powder (Piccard).

Phloroglucolsulphonic Acid, $\text{C}^6\text{H}^3\text{SO}^6 = \text{C}^6\text{H}^3\text{O}^3(\text{SO}^2\text{H})$, produced by the action of pyrosulphuric acid on phloroglucol, forms very soluble salts with the alkalis and alkaline earths, and is coloured deep violet by baryta-water and ferric chloride. By the action of phosphorus oxychloride, it is converted into an amorphous anhydride which may be purified by washing it, first with ether, then repeatedly with water, and finally dissolved in water at 50° – 60° . The resulting yellow solution reacts with albumin, gelatin, alkaloids, acids, salts, and iodide of starch, exactly like tannic acid. It is precipitated by hydrochloric acid, and on repeating this operation several times, there is obtained a yellow precipitate of the formula $\text{C}^{12}\text{H}^{10}\text{S}^2\text{O}^{11} = 2\text{C}^6\text{H}^3\text{SO}^6 - \text{H}^2\text{O}$, which dissolves readily in water, and when boiled with dilute acids is reconverted into phloroglucolsulphonic acid, which exhibits none of the reactions of tannic acid. Lastly, there is precipitated a highly carbonised body, $\text{C}^{12}\text{H}^{10}\text{S}^2\text{O}^{13}$, which also reacts like tannin, but does not decolorise iodide of starch. This body may be formed from the sulphonic acid of phloroglucide according to the equation $2\text{C}^{12}\text{H}^{10}\text{O}^5(\text{SO}^2\text{H}) - \text{H}^2\text{O} = \text{C}^{12}\text{H}^{10}\text{S}^2\text{O}^{13}$ (H. Schiff, *Ber.* vi. 26).

PHLOROL, $\text{C}^6\text{H}^{10}\text{O} = \text{C}^6\text{H}^3(\text{OH})$. This phenol, first noticed as a constituent of beech-tar creosote by Marasse (vi. 928), and afterwards by Tiemann a. Mendelsohn (p. 580 of this volume), has been further examined by the last-mentioned chemists (*Ber.* x. 57). To determine its constitution, it was first converted into methyl-phlorol, for which purpose the ether-alcoholic mother-liquors, obtained in the preparation of potassium-creosol from the portion of the creosote boiling between 200° and 230° , were evaporated on the water-bath; the aqueous residue was acidulated with hydrochloric acid and exhausted with ether; and the ethereal extract was evaporated, whereby an oil (b. p. 220°) was obtained which was boiled for several hours in a reflux apparatus with potassium hydrate, methyl iodide, and methyl alcohol. On heating the product of this reaction over the water-bath to remove methyl alcohol, and then adding water, an oil was obtained separable by rectification into two portions, one boiling at 215° , the other at about 200° . The latter, which is the crude methyl-phlorol, gave, when suspended in 20 pts. water and boiled in a reflux apparatus with potassium permanganate (1 : 40), a mixture of acids, which was fused for a short time with potassium hydrate to remove the methyl-groups contained in it; and the substance afterwards separated from the melt by hydrochloric acid, was found to be identical with hydroxyphthalic or hydroxybenzene-orthodicarboxylic acid, $\text{C}^6\text{H}^3(\text{OH})(\text{COOH})^2$ (p. 1531). From these results, Tiemann a. Mendelsohn infer that the phlorol of beech-tar is a hydroxy-xylene, $\text{C}^6\text{H}^3(\text{CH}^3)_2\text{OH}$. The phlorol prepared by distillation of calcium phlorotate (p. 1569) they regard as an ethylphenol.

PHLOROSE, $\text{C}^6\text{H}^{12}\text{O}^6$. A sugar obtained by the action of sulphuric acid on phlorizin (see SUGARS).

PHOLERITE. A mineral from India, named *Meerschallummite* by Ross, has been shown by Maskelyne a. Flight (*Chem. News*, xxii. 260) to contain 43.144 per cent. SiO^2 , 41.073 Al^{12}O^3 , and 16.783 H^2O , and to be identical with pholerite (iv. 496).

Frenzel regards the pholerite, nacrite, and lithomarge of the Saxon and Bohemian tin-mines as varieties of gilbertite (p. 860).

PHONOLITE. The following are analyses of this volcanic rock: (1 and 2). From the Wolf Rock near the Land's End, Cornwall: exhibits small sanidins enclosed in a compact grey matrix. Sp. gr. 2.54 (Allport, *Jahrb. f. Min.* 1874, 38; analysed by A. Phillips). (3). From the Ravin de l'Uclade, Auvergne. Sp. gr. 2.54. Analysed by C. v. Bonhorst (*ibid.* 1872, 337). (4 and 5). Nosean-phonolites from the Hohentwiel in the Högau. 4. Fresh rock: 55.9 per cent. soluble; 44.1 insoluble. Sp. gr. 2.54. 5. Weathered: 39 per cent. soluble; 61 insoluble. Sp. gr. 2.41:

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	FeO	CaO	MgO	K ^a O	Na ^a O	H ^a O	
1.	56.46	22.29	2.70	0.97	1.47	—	2.81	11.13	2.05	= 99.88
2.	56.40	22.20	2.61	0.97	1.35	—	2.73	11.11	2.05	= 99.42
3.	59.84	23.07	3.35	—	1.48	0.25	4.13	4.62	3.20	= 99.84
4.	55.21	21.78	2.06	2.01	2.10	0.13	3.475	10.64	2.07	= 99.475
5.	55.84	19.87	2.58	1.55	—	1.81	6.23	8.06	3.87	= 90.81

PHORONE, C⁹H¹⁰O. This name has been given to at least two isomeric bodies, one, which is the ketone of camphoric acid (also called *camphorone*) being formed by distillation of calcium camphorate (i. 733; vii. 949), the other (also called *acephorone*) being produced by the condensation of acetone under the influence of strong hydrochloric acid: 3C³H⁶O = C⁹H¹⁰O (i. 23; vi. 26); and by heating nitrosotriacetoneamine (p. 29) with potash:



The action is best commenced over the water-bath, and completed by boiling the liquid in a reflux apparatus, and the phorone thus produced may be extracted with ether and purified by distillation (Heintz, *Liebig's Annalen*, clxxxvii. 250).

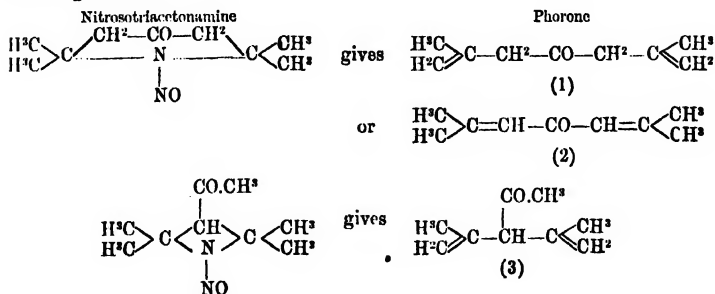
Camphorone is a liquid boiling at 208° (Gerhardt); at 206°–215° (Kachler); acephorone crystallises in large yellowish prisms, melts at 28°, boils at 190°–191° (Claisen, *Liebig's Annalen*, clxxxiv. 163).

The phorone produced by the action of alkaline reagents on acetone (i. 29) appears to be identical with camphorone. A liquid having the composition of phorone, and boiling at 230°–235°, is obtained, together with camphor, by distilling the calcium salt of camphic acid with calcium formate (J. de Montgolfier, *Compt. rend.* lxxxviii. 515).

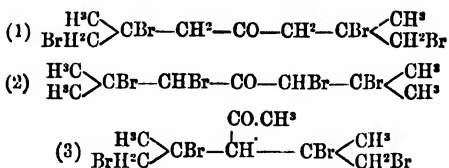
Acephorone is very readily attacked by *oxidising agents*; dilute nitric acid converts it into acetic and oxalic acids. By dehydration with *phosphoric anhydride*, it is converted chiefly into pseudocumene, C⁹H¹² (p. 1284). Its solution in carbon sulphide readily absorbs *bromine*, forming a well-crystallised tetrabromide, C⁹H¹⁰O.Br₄, easily soluble in ether, sparingly in cold water, melting at 86°–88°. With *sodium-amalgam* acephorone yields only imperfectly crystallised resinous products; but when its alcoholic solution is left in contact with zinc and sulphuric acid, it takes up hydrogen and is converted into deoxyphorone, C⁹H¹²O, related to it in the same manner as pinacolin to acetone, and deoxybenzoin to benzaldehyde. This compound crystallises in short colourless four-sided prisms, melts at 108°, sublimes well, and volatilises easily with vapour of water. The same compound is formed by treating the above-mentioned tetrabromide with zinc and hydrochloric acid. By strong *sulphuric acid*, acephorone is for the most part converted into mesitylene (Claisen, *Ber.* xi. 1168; *Liebig's Annalen*, clxxx. 1).

Acephorone unites with *hydriodic acid*, forming the compound C⁹H¹²I₂O, which crystallises in needles, melts at 13°, is partly decomposed by boiling, but not decomposed by water, and is reconverted into phorone by alcoholic potash (Kasaneff, *Ber.* viii. 435).

Camphorone being the ketone of camphoric acid, probably forms a closed chain, as represented by Kachler's formula (vii. 949); but acephorone, according to the preceding reactions and its formation from nitrosotriacetoneamine by removal of N₂ and H₂O (p. 1572), appears to have the constitution of an open chain with two double linkings. The two formulæ of nitrosotriacetoneamine give for phorone the three following formulæ:



Either of these three phorone-molecules with two pairs of doubly linked carbon-atoms may take up 4 at. bromine, and form the tetrabromide, which may accordingly be represented by one of the three following formulæ:



PHORONIC ACID, $\text{C}^6\text{H}^{16}\text{O}^2$. A crystallisable acid, obtained under certain circumstances by oxidation of camphic acid with potassium permanganate (Montgolfier, *Compt. rend.* lxxxv. 961), the usual product being hydroxycamphic acid, $\text{C}^{10}\text{H}^{18}\text{O}^3$ (p. 372).

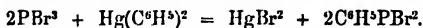
PHOSENE, or **PHOTENE**. According to Barbier (*Ann. Chim. Phys.* [5], vii. 526), the substance so-called by Fritzsche (vi. 176) is a mixture of anthracene and phenanthrene.

PHOSGENITE. A mineral discovered by Sella in the lead mines of Monte Poni; found also at Gibbus. The crystals are hexagonal, exhibiting the combination $\infty \text{P} . \infty \text{P}2 . 0\text{P} . 2\text{P}2 . 2\text{P}\infty . \infty \text{P}\infty$, the faces ∞P being vertically striated. Axial ratio $a : c = 1 : 1.08758$ (Hansel, *Jahrb. f. Min.* 1878, 754).

PHOSPHAM. This name is given to the nitril of phosphoric acid, PHN^2 , which Rose obtained by passing ammonia gas over phosphorus pentachloride and heating the product in a stream of carbon dioxide (iv. 497). M. Salzmann (*Ber.* vii. 494), by passing ammonia gas over moderately heated phosphorus pentachloride, obtained a product which, after successive treatment with hot water, hydrochloric acid, potash, and ether, formed a white amorphous powder scarcely acted upon by acids or alkalis, and giving by analysis numbers leading to the improbable formula $\text{P}^3\text{H}^4\text{N}^2$, possibly a mixture of several compounds.

PHOSPHANILATE, DIPHENYLIC, $\text{C}^{18}\text{H}^{16}\text{NPO}^3 = \text{PO} \left\{ \begin{array}{l} (\text{OC}^6\text{H}^3)^2 \\ \text{NH.C}^6\text{H}^3 \end{array} \right.$ (Wallach a. Heymer, *Ber.* viii. 1235). This ether is obtained by dropping a mixture of equal parts of phenol and aniline on the calculated quantity of phosphorus pentachloride, and treating the semi-solid product with water and soda-ley. It crystallises in six-sided tablets melting at $127^\circ\text{--}128^\circ$; dissolves both in acids and in alkalis, sparingly in water, readily in alcohol and ether; has a neutral reaction, and is decomposed by distillation, giving off aniline and phenol.

PHOSPHENYL BROMIDES (Michaelis a. Köhler, *Ber.* ix. 519). The *Dibromide*, *Phosphorus Phenyldibromide*, or *Phosphorus Dibromophenide*, $\text{C}^6\text{H}^3\text{PBr}^2$, is formed by passing hydrogen bromide dried with phosphoric anhydride into boiling phosphenyl dichloride (*infra*), whereupon the gas is completely absorbed, streams of hydrochloric acid gas carrying benzene with them are given off, and small quantities of phosphorus separate out. The product, after saturation with hydrogen bromide and rectification in a stream of carbon dioxide, consists essentially of phosphenyl dibromide, together with small quantities of phosphorus chloride and bromide, monobromobenzene, and diphenyl. It may be freed from dissolved phosphorus by heating it to $250^\circ\text{--}300^\circ$ in a sealed tube, the phosphorus then separating out in the red amorphous state. The diphenyl is very difficult to remove. Phosphenyl dibromide may, however, be obtained free from diphenyl, but in small quantity only, by the action of phosphorus bromide on mercury-diphenyl:



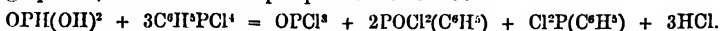
Phosphenyl dibromide is a colourless liquid, boiling at $255^\circ\text{--}257^\circ$; it soon turns yellow, and on exposure to sunlight becomes turbid and deposits a red substance. It is decomposed by water into hydrobromic acid, phosphenylic acid, and phenyl-phosphine.

Phosphenyl Tetrabromide, *Phosphoric Phenyltetrabromide* or *Tetrabromophenide*, $\text{C}^6\text{H}^3\text{PBr}^4$, formed, with great rise of temperature, by direct combination of the dibromide with bromine, is a yellow-red mass which, when heated, sublimes in yellow-red needles melting at 207° . It fumes strongly in the air, and is converted by water into hydrobromic and phosphenylic acids. It unites with bromine, forming a *hexabromide*, $\text{C}^6\text{H}^3\text{PBr}^6$, which sublimes at 110° in dark-red needles, and is decomposed by water, yielding bromine, hydrobromic acid, and phosphenylic acid.

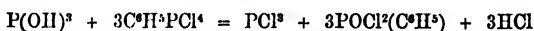
PHOSPHENYL CHLORIDES. *Dichloride*, *Phosphorus Phenyl-dichloride* or *Dichlorophenide*, $\text{C}^6\text{H}^3\text{PCl}^2$.—To prepare this compound, the mixed vapours of benzene and phosphorus trichloride are passed through a hot tube filled with fragments of pumice, the vapour of that portion of the condensed liquid which distilled below 80° being again repeatedly passed through the tube; and the

portion of the product which boils above 80° is subjected to fractional distillation. Phosphenyl dichloride thus obtained is a colourless, very stable, strongly refractive liquid, having a sp. gr. of 1.319 at 20° , and boiling at 222° (Michaelis, *Ber.* vi. 601, 816). It is converted by chlorine into phosphenyl tetrachloride, by hydrogen iodide into phosphenyl di-iodide, by oxygen and sulphur into phosphenyl oxychloride and sulphochloride respectively, by cooled zinc-ethyl into diethylphenylphosphine, $P(C^6H^5)_2(C^2H^5)$.

Phosphenyl Tetrachloride, *Phosphoric Phenyl-tetrachloride* or *Tetrachlorophenide*, $C^6H^5PCl_4$, is obtained, by passing chlorine into the dichloride well cooled by cold water, as a dry mass, the yellow colour of which is due to excess of chlorine, and may be removed by crystallisation from phosphorus trichloride or phosphenyl dichloride. It melts at 73° to a clear liquid which solidifies to a crystalline mass on cooling. At a higher temperature it partly sublimes unaltered and is partly resolved into the dichloride and free chlorine (Michaelis, *loc. cit.*) When heated in a tube, it exhibits no alteration at 100° , but melts at 140° , and is resolved at 180° into PCl_3 , boiling at 78° , monochlorobenzene, and other products boiling at higher temperatures (Michaelis a. Kammerer, *Ber.* viii. 1306). Water decomposes it with violent hissing, forming at first phosphenyl oxychloride as an oily liquid, which is further converted into phosphenylic acid (Michaelis). With phosphorous acid, it yields phosphenyl dichloride and oxychloride in the quantities required by the following equation, without a trace of phosphorus trichloride:



This tends to show that phosphorous acid has the constitution represented by $OPH(OH)^2$, since if it were correctly represented by the formula $P(OH)^3$, it should yield with phosphenyl tetrachloride, not phosphenyl oxychloride and dichloride together with phosphorus oxychloride, but phosphenyl oxychloride and phosphorus trichloride: thus



(Michaelis a. Ananoff, *Ber.* vii. 994). With *phenol*, phosphenyl tetrachloride gives off hydrochloric acid, and yields, together with monochlorobenzene, white needles of phenyl phosphonylate, $C^6H^5PO^2(C^6H^5)^2$ (Michaelis a. Kammerer, *Ber.* viii. 1306).

Phosphenyl Chlorobromide, $C^6H^5PCl^2Br$, is obtained by adding 1 mol. bromine to 1 mol. well-cooled phosphenyl dichloride, as a dry yellow-red solid mass which melts at about 208° to a dark-brown liquid, but sublimes even at 130° without decomposition in fan-shaped groups of yellow-red crystals. With a sufficient quantity of water it yields, as final products, hydrochloric, hydrobromic, and phosphenylic acids (Michaelis).

Phosphenyl Chlorotetrabromide, $C^6H^5PCl^2Br_3$, is formed, with brisk reaction, on adding 1 mol. bromine to the chlorobromide just described. The mixture, which is pasty at first, quickly solidifies to a dry bright-red mass which is decomposed by water, yielding phosphenylic, hydrochloric, and hydrobromic acids, and free bromine (Michaelis).

Phosphenyl Oxychloride, $C^6H^5PCl^2O$, is formed by direct combination of oxygen with phosphenyl chloride, the action being greatly facilitated by heat; also by the action of oxalic acid, and of phosphorous acid (*supra*) on phosphenyl tetrachloride. It is a colourless thickish liquid, having a faint odour, a density of 1.375 at 20° , and boiling, not quite without decomposition, at 260° (uncorr.) By water it is slowly resolved into hydrochloric and phosphenylic acids (Michaelis).

Phosphenyl Thiochloride, $C^6H^5PCl^2S$.—Sulphur dissolves quietly in phosphenyl dichloride at ordinary temperatures, but on heating the solution, it suddenly assumes a darker colour, and the two substances enter into chemical combination, attended with violent ebullition, and when considerable quantities are present, with inflammation. The thiochloride thus formed is a colourless liquid, boiling under ordinary pressure at 270° , with partial decomposition; under a pressure of 130 mm. at 205° . Sp. gr. = 1.376 at 13° . Its odour is aromatic at ordinary, pungent at higher temperatures. It fumes slightly in the air, and is decomposed by prolonged boiling with water, into hydrochloric, hydrosulphuric, and phosphenylic acids. Strong potash-ley attacks it violently; dilute potash-ley only after prolonged boiling. On evaporating the resulting solution and treating the residue with alcohol, potassium chloride remains undissolved, and a salt which crystallises in small needles, and probably consists of potassium thiophosphenylate, $C^6H^5PS(OK)^2$, passes into solution. The alcoholic solution thus formed acquires when somewhat concentrated an odour like that of mercaptan. The corresponding lead salt is a white precipitate, which blackens when boiled with water (Köhler a. Michaelis, *Ber.* ix. 1053).

PHOSPHENYL DIODIDE, $C^6H^5PI_2$, is formed, with rapid evolution of hydrogen chloride, when dry hydrogen iodide is passed into the corresponding chloride (p. 1574). The liquid becomes heated and darker in colour, begins to deposit a crystalline body, then gradually becomes thicker, and finally solidifies completely to a dry dark-coloured mass, which still for awhile rapidly absorbs hydrogen iodide. The iodide of phosphenyl and hydrogen thus formed distils, with copious evolution of hydrogen iodide, at a temperature above the boiling point of mercury, and is decomposed by water and more readily by alcohol, yielding phenyl-phosphine, $PH(C^6H^5)$.

PHOSPHENYL SULPHIDES. Köhler a. Michaelis (*Ber.* x 815), by treating phosphenyl dichloride, heated nearly to boiling, with dry hydrogen sulphide, obtained a thick, colourless, disagreeably-smelling liquid, very much like the sulphide of phenyl-phosphine, and having the composition C^6H^5PS . This substance, heated with nitric acid, yields diphenylphosphinic acid, together with phosphoric acid; hence its constitution is probably $(C^6H^5)_2P.S.PS$. Köhler a. Michaelis call it *isophosphenyl sulphide*. Together with this compound, which dissolves readily in ether, there is also formed *tetraphenylphosphotrisulphide*, $(C^6H^5)_4P^2S_3$, which crystallises from warm ether in white crystals melting at 192° – 193° , and yielding by oxidation diphenylphosphinic acid.

PHOSPHENYLIC ACID, $C^6H^5.PO(OH)_2$. *Phenyl-phosphoric*, *Phenyl-phosphinic*, or *Benzenephosphinic Acid* (Michaelis, *Ber.* vi. 816; Michaelis a. Mathias, *ibid.* vii. 1070). This acid is the final product of the decomposition by water of all the derivatives of phosphenyl dichloride above described. It is best prepared by adding phosphenyl tetrachloride in successive small portions to water, and warming the liquid for some time to complete the decomposition of the phosphenyl oxychloride formed in the first instance. On evaporating the resulting solution which contains hydrochloric acid, the phosphenylic acid crystallises in colourless clinorhombic laminæ having a vitreous lustre. In pure water the acid is much more soluble, so that the solution requires to be much more highly concentrated before it will begin to crystallise, the whole then solidifying to a pulp of small felted laminæ, enclosing a large quantity of mother-liquor. 100 pts. by weight of water at 15° dissolve 23.5 pts. of the crystallised acid; it dissolves readily also in alcohol. It melts at 158° , and when quickly heated to about 250° is resolved into benzene and metaphosphoric acid, a decomposition exactly analogous to that of tribasic phosphoric acid into metaphosphoric acid and water, and to that of aromatic carboxylic acids into CO_2 and hydrocarbons.

Phosphenylic acid slowly heated above its melting point gives off water, and leaves a residue of condensed phosphenylic acids. At 200° , two mols. of $C^6H^5.PO(OH)_2$ lose 1 mol. H_2O , leaving di- or pyro-phosphenylic acid, $(C^6H^5)_2(PO)_2O(OH)_2$, and at 210° three mols. of the acid are converted, by loss of $2H_2O$, into triphosphenylic acid, $(C^6H^5)_3(PO)_3O(OH)_2$.

1 mol. phosphenylic acid heated to 100° in a sealed tube with 1 mol. bromine in presence of water, yields—together with a small quantity of oil and unaltered phosphenylic acid—paradibromobenzene (m. p. 89°), hydrobromic acid, and phosphoric acid (Benzinger a. Michaelis, *Ber.* viii. 550).

Phosphenylates.—Phosphenylic acid is a powerful bibasic acid, forming acid and neutral salts. The free acid precipitates neither barium chloride nor silver solutions, but on addition of a little ammonia, white precipitates are thrown down. The addition of sodium acetate also determines the precipitation of the silver salt.

The *neutral potassium salt*, $C^6H^5PO^3K^2$, is uncrystallisable and very soluble. The *acid salt*, $C^6H^5PO^3KH$, is precipitated from its aqueous solution by alcohol as a crystalline powder. *Neutral sodium phosphenylate*, $C^6H^5PO^3Na^2.12H_2O$, resembles the corresponding sodium phosphate. The *acid salt* crystallises less easily in similar forms.

Calcium phosphenylate, $C^6H^5PO^3Ca.2H_2O$, is a white, amorphous precipitate, soluble though with difficulty, in acetic acid. By evaporating this solution, the *acid salt*, $(C^6H^5PO^3)_2H^2Ca^2$, is obtained, crystallised in beautiful shining scales, which are anhydrous. The *acid strontium salt*, $(C^6H^5PO^3)_2H^2Sr.H_2O$, resembles the calcium salt. *Zinc phosphenylate* has the formula $C^6H^5PO^3Zn.H_2O$. *Copper phosphenylate* is $C^6H^5PO^3Cu$. *Silver phosphenylate*, $C^6H^5PO^3Ag^2$, is a light white powder, not changed by light. *Ferric phosphenylate*, $(C^6H^5PO^3)_3Fe^2.2\frac{1}{2}H_2O$, is a yellowish white precipitate.

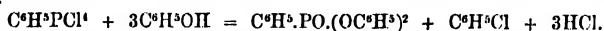
Phosphenylic Ethers. *Ethyl-phosphenylic acid*, $C^6H^5.PO(OC^2H^5)(OH)$, is formed on adding phosphenyl tetrachloride to absolute alcohol, and leaving the solution to evaporate first on the water-bath, then over lime. It is a thick, heavy,

oilily, non-volatile liquid having a fruity odour, and is quickly decomposed by water into alcohol and phosphenylic acid. Its *silver salt*, $C^6H^5.PO(OC^2H^5)(OAg)$, separates, on mixing the alcoholic solutions of the free acid and silver nitrate, as a yellowish-white precipitate, quickly blackening on exposure to light; it is quickly decomposed by water, with separation of phosphenylic acid and silver phosphenylate; ammonia and nitric acid dissolve it readily, though not without decomposition (Michaelis a. Mathias).

Ethylphosphenylic acid is also formed by the action of water on the normal ether (*infra*). It unites with water, forming an unstable hydrate consisting of scaly crystals, which liquefy and give off their water even over sulphuric acid at ordinary temperatures. By prolonged contact with water, the acid ether is converted into phosphenylic acid (Köhler a. Michaelis, *Ber.* x. 816).

Normal Ethyl Phosphenylate, $C^6H^5P(OC^2H^5)^2$, is formed by the action of sodium ethylate on phosphenylic dichloride. The reaction is rather violent, so that it is best to drench the sodium ethylate with ether, and gradually add the phosphenylic chloride, keeping the retort well cooled. This ether is a colourless, very mobile liquid, having an intensely disagreeable odour, a density of 1.032 at 16°, and boiling at 235°.* It is insoluble in water, and is gradually decomposed thereby, yielding alcohol and ethylphosphenylic acid (Köhler a. Michaelis).

Phenyl Phosphenylate, $C^6H^5.PO(OC^2H^5)^2$, is formed, together with monochlorobenzene and hydrochloric acid, by the action of phosphenylic tetrachloride on phenol:



It crystallises in thin white needles melting at 63.5°; is insoluble in water, but dissolves readily in alcohol, ether, and benzene; is scarcely attacked by aqueous potash, but easily resolved by hot alcoholic potash into phenol and phosphenylic acid.

Phenyl phosphenylate is also formed, together with the chloride, $C^6H^5.PO(OC^2H^5)Cl$, by the action of phosphorus oxychloride on phenol. This chloride is converted by boiling water into phenylphosphenylic acid, $C^6H^5.PO(OH)(OC^2H^5)$, and may thus be separated from the normal ether. The acid ether forms long capillary needles melting at 57°, dissolves sparingly in water, easily in alcohol, ether, benzene, and alkalis. Its ammonium salt forms colourless needles; the silver salt needles having a silky lustre (Michaelis a. Kammerer, *Ber.* viii. 48).

Nitrophosphenylic Acid, $C^6H^5(NO_2).PO(OH)^2$, is obtained by heating phosphenylic acid to 100° with fuming nitric acid, and purified from unaltered phosphenylic acid by conversion into the barium salt (*infra*). It crystallises from ether in radiate groups of white needles, from water in cauliflower-like masses; deliquesces in moist air; melts at 132°, resolidifies at 105°, and explodes when heated above 200°.

The *normal barium salt*, $C^6H^5(NO_2).PO.O^2Ba + 2H^2O$, is prepared by agitating the cold solution of the crude acid with barium carbonate, filtering, and treating the undissolved substance with cold water as long as the filtrate gives a reaction of barium. Nitrophosphenylate of barium then dissolves, while the phosphenylate remains behind. This salt is more soluble in cold than in hot water, 100 pts. water dissolving 0.844 pts. of it at 22° and 0.646 at 100°. The *acid barium salt*, $(C^6H^5NO_2PO)^2Ba + 2H^2O$, crystallises in white laminae much more soluble than the normal salt. The *calcium salt*, $C^6H^5(NO_2).PO.O^2Ca + \frac{1}{2}H^2O$, is a yellowish-white amorphous powder. The *silver salt*, $C^6H^5(NO_2).PO.(OAg)^2$, obtained by precipitation, is a yellowish-white powder, easily soluble in ammonia and in nitric acid, sparingly in water, and separating therefrom in white laminae. The *lead salt*, $C^6H^5(NO_2).PO.O^2Pb$, is a white pulverulent precipitate.

Solutions of sodium nitrophosphenylate give with ferric chloride a reddish, with cupric sulphate, on warming, a green flocculent precipitate; with cobalt nitrate a violet precipitate; with mercuric, bismuth, and zinc solutions, white precipitates (Michaelis a. Benziger, *Ber.* viii. 1310; *Lieb. Ann.* clxxxviii. 275).

Amidophosphenylic Acid, $C^6H^5(NH^2).PO(OH)^2$ (Michaelis a. Benziger, *Ber.* ix. 513; *Lieb. Ann.* clxxxviii. 275). When nitrophosphenylic acid is treated with tin and hydrochloric acid, stannous nitrophosphenylate first separates as a bulky yellow precipitate, which is subsequently reduced to amidophosphenylate; and the liquid freed from tin by hydrogen sulphide leaves on evaporation a red viscid mass, from which, by washing with alcohol, amidophosphenylic acid is obtained as a greyish-white powder.

This acid, when recrystallised from hot water, forms thin, white, glistening

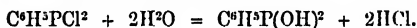
* In a former paper by Benziger a. Michaelis (*Ber.* viii. 1310), it is stated that normal ethyl phosphenylate obtained by the action of ethyl iodide on silver phosphenylate, boils at 267°, and the methyl ether similarly prepared at 247°.

needles, which at 280° acquire a bluish-green colour, and undergo decomposition 100 pts. of water dissolve 0.43 pt. of the acid at 20° , and 0.52 pt. at 100° ; in alcohol. it dissolves but sparingly, and in ether not at all. Heated with soda-lime, it yields aniline and phosphoric acid. It dissolves readily in hydrochloric acid, forming a solution which is coloured permanently red by bleaching-powder.

Sodium Amidophosphenylylate, $C^6H^4(NH^2)PO^3Na^2 + 3H^2O$, obtained by reducing the nitro-acid with sodium-amalgam, crystallises in white prisms, which effloresce over sulphuric acid. The *silver salt*, $C^6H^4(NH^2)PO(OAg)^2$, is a pale yellow precipitate, freely soluble in ammonia and nitric acid. The *copper salt*, $C^6H^4(NH^2)PO^3Cu$, is a bluish-green powder soluble in acetic acid. The *lead salt*, $C^6H^4(NH^2)PO^3Pb$, is a white amorphous precipitate.

Diazophosphenylic Acid. When a hot solution of the amido-compound in nitric acid is treated for some time with nitrous acid and then concentrated, the nitrate of diazophosphenylic acid, $C^6H^4N^2.NO^3PO^3H^2 + 3H^2O$, separates out, and may be purified by pressing and crystallisation from nitric acid. It forms white prisms, is freely soluble in water and alcohol, sparingly in ether. It contains three molecules of water. It gives off 2 mols. H^2O at 130° , melts at 188° , and explodes at a few degrees higher. The *potassium salt*, $C^6H^4N^2O^3PO^3K^2 + H^2O$, is obtained as a precipitate consisting of small yellow needles. The *barium salt*, $C^6H^4N^2O^3PO^3Ba + 3H^2O$, crystallises from water in reddish-yellow glistening needles, which lose their water at 130° ; it is very explosive. The *silver salt*, $C^6H^4N^2O^3PO^3Ag^2$, is a red, amorphous, very sparingly soluble powder. The *lead salt*, $C^6H^4N^2O^3PO^3Pb$, is a yellow powder. The aqueous solution of the free acid is very stable, and does not give off nitrogen on boiling; it does not show the reaction of nitric acid until boiled with an alkali (Michaelis a. Benziger, *loc. cit.*)

PHOSPHENYLOUS ACID, $C^6H^5PO^2 = C^6H^5.P(OH)^2$ (Michaelis a. Ananoff, *Ber.* vii. 1688). This acid is formed when phosphenyl dichloride is allowed to drop gradually into water, and separates on heating the liquid product to boiling, and filtering, either as an oil or in white leaflets:



100 pts. of boiling water dissolve 211 pts. of phosphenylyous acid, while 100 pts. of cold water dissolve only 7.23 pts. The acid is readily soluble in alcohol, and melts at 70° , but decomposes at a higher temperature (170° – 250°) in accordance with the equation



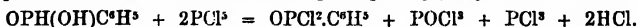
Probably this decomposition takes place in two stages, thus:—

- (1). $3C^6H^5P(OH)^2 = C^6H^5PH^2 + 2C^6H^5PO(OH)^2$.
- (2). $C^6H^5PO(OH)^2 = PO^3H + C^6H^5$.

Phosphenylyous acid is monobasic, and reduces mercuric chloride to calomel, sulphurous acid to sulphur, and silver nitrate to the metallic state.

The following salts have been obtained:— $C^6H^5PO^2KH + 2H^2O$, deliquescent needles; $C^6H^5PO^2H(NH^4)$, deliquescent rhombic tables; $(C^6H^5PO^2H)^2Ca$, foliated crystalline mass; $(C^6H^5PO^2H)^2Ba + 4H^2O$, shining rhombic crystals; $(C^6H^5PO^2H)^2Pb$, slightly soluble needles; $(C^6H^5PO^2H)^2Fe$, white amorphous precipitate.

When phosphenylyous acid is treated with phosphorus pentachloride, an action takes place, resulting in the formation of phosphenyl oxychloride, thus:



This reaction points to the conclusion that phosphenylyous acid is correctly represented by the constitutional formula $OPH(OH)C^6H^5$, and phosphorous acid by the corresponding formula $OPH(OH)^2$, as already inferred from the action of that acid on phosphenyl tetrachloride (p. 1575).

When phosphenylyous acid is subjected to the action of *chlorine*, the H-atom attached to the phosphorus is not replaced by chlorine, but a brisk reaction takes place, resulting in the formation of pyrophosphenylyous acid and phenyl-phosphine, the latter being subsequently carbonised by the excess of chlorine.

PHOSPHIDES. On Hydrogen Phosphide, see PHOSPHINES.

Metallic Phosphides.—Many of these compounds are decomposed by heat, and cannot therefore be obtained by the action of phosphorus on metals at high temperatures under ordinary atmospheric pressure. Complete union, however, may frequently be effected by heating the metals in the form of wire or foil with phosphorus in sealed glass tubes, protected by enclosing them in iron tubes filled with

magnesia, a dull red heat being kept up for eight to ten hours, and the tubes being opened in an atmosphere of carbon dioxide.

Copper phosphide, CuP , thus prepared, is a pulverulent silvery mass, of sp. gr. 5.14, insoluble in hydrochloric acid, oxidised by nitric acid. *Magnesium phosphide* is a bluish-green very unstable substance, oxidising rapidly to phosphate on exposure to the air. *Silver phosphide*, AgP , is black and very brittle; leaves metallic silver when ignited. *Cadmium phosphide*, Cd^2P , is a greyish or sometimes silver-white mass, dissolving in hydrochloric acid with evolution of phosphine. *Zinc phosphide*, Zn^3P^2 , is a crystalline mass. No other phosphide of zinc was obtained by the process above described (comp. v. 1073; vi. 1134; vii. 1214).

Tin phosphides, SnP , and SnP^2 , were obtained according to the proportion of phosphorus used. The first is tin-white; the second black and brilliant, and splits into thin plates. Sp. gr. of $\text{SnP}^2 = 4.91$ at 12° . This compound is not attacked by hydrochloric acid. Aluminium and mercury were not attacked when heated with phosphorus as above described; iron only superficially (Emmerling, *Ber.* xii. 152).

On the preparation of Metallic Phosphides by precipitation, see vii. 949.

PHOSPHINES. *Phosphine*, or *Gaseous Hydrogen Phosphide*, PH^3 , may be obtained in the pure state by decomposing phosphonium iodide with water, or by the action of sodium ethylate on phosphorus in alcoholic solution; aqueous or alcoholic solutions of ammonia yield only traces of phosphine. The formation of spontaneously inflammable phosphine by the action of aqueous alkalis on phosphorus is not prevented by the presence of glycerol.

Phosphine reduces *sulphuric acid* with extraordinary energy, but without at first producing any visible alteration; as soon however as the acid is saturated with the gas, it suddenly becomes so hot that the phosphine is set on fire. If the liquid be cooled, sulphurous acid is formed and sulphur deposited. With an alcoholic solution of *mercuric cyanide*, phosphine produces a yellow precipitate extremely sensitive to light and containing mercury, cyanogen, phosphorus, and hydrogen. A similar, but red-brown, and still more easily alterable precipitate, is formed in an alcoholic solution of mercuric cyanide by *arsine*, AsH^3 . *Stibine*, SbH^3 , reduces mercuric cyanide even more energetically, throwing down nothing but metallic mercury (W. R. Hodgkinson, *Chem. News*, xxxiv. 14, 67, 167).

Phosphine is slowly decomposed by *sulphur* in sunshine, yielding reddish-yellow phosphorus sulphide and hydrogen sulphide: $2\text{PH}^3 + 6\text{S} = \text{P}^2\text{S}^3 + 3\text{H}^2\text{S}$ (F. R. Jones, *Chem. Soc. J.* xxix. 618).

On the preparation of *Phosphine Hydriodide*, or *Phosphonium Iodide*, PH^4I , see A. W. Hofmann (vii. 931). On the reaction which takes place in the formation of this compound, see K. Lissenko (*Ber.* ix. 1313; *Chem. Soc. J.* xxxi. 46).

Liquid Hydrogen Phosphide, P^2H^4 .—The following method of preparing this compound for lecture experiments is described by Hofmann (*Ber.* vii. 531). A thick-walled U-tube, three or four millimeters in diameter, and provided with a stop-cock on each arm, is surrounded by a freezing mixture (16° to 20°), and receives the phosphoretted hydrogen prepared from 30 to 50 grams of freshly made calcium phosphide. A wide glass tube in the cork of the generating flask, dipping beneath the surface of the water (at about 60°), serves for the introduction of the phosphide. While the liquid is being collected, spontaneously inflammable phosphoretted hydrogen escapes; and on displacing this by a stream of carbon dioxide, the bright flame is replaced by a scarcely luminous green flame, of so low a temperature that a taper cannot be lighted at it. This flame is caused by the liquid phosphoretted hydrogen in the stream of carbon dioxide coming in contact with the air. The carbon dioxide may be replaced by a stream of some combustible gas, e.g. hydrogen, and a luminous flame again obtained.

On Isopropyl-, Isobutyl-, and Isopentyl- or Amyl-phosphines, see vii. 955.

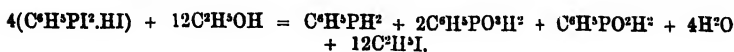
Trimethylphosphine Hydriodide, $\text{P}(\text{CH}^3)^3\text{HI}$, is formed by heating 1 pt. carbon disulphide with 3 pts. phosphonium iodide in a sealed tube at 150° :



On cooling, the contents of the tube solidify to a brown crystalline mass mixed here and there with red needles; and this product, mixed with soda-ley and agitated with ether, yields trimethylphosphine with all its characteristic properties (iv. 609). The red crystals contain phosphorus, sulphur, and iodine (Drechsel, *J. pr. Chem.* [2], x. 180).

Phenylphosphine, $\text{C}^6\text{H}^5\text{PH}^3$. *Phosphaniline* (Michaelis, *Ber.* vii. 6; Köhler a. Michaelis, *ibid.* x. 807). This base is formed, together with phosphenylic and

phosphenylic acids, by the action of alcohol on phosphenyl-hydrogen iodide, according to the equation,



the phosphenylic acid being further resolved on heating into phosphenylic acid and phenylphosphine :



The residue left after distilling off the alcohol yields, when heated above 250° , a mixture of water, benzene, and phenylphosphine, the phosphenylic acid being first resolved into water and pyrophosphenylic acid, $2\text{C}^6\text{H}_5\text{PO}^2\text{H}^2 = \text{H}^2\text{O} + (\text{C}^6\text{H}_5)_2\text{P}^2\text{O}^2$, and the latter at higher temperatures into benzene and P^2O^5 , which with the water forms metaphosphoric acid. Phenylphosphine may also be prepared by adding phosphenyl dichloride (p. 1575), holding phosphorus in solution, gradually, and with agitation, to excess of alcohol, and distilling the filtrate in a stream of carbon dioxide.

Phenylphosphine is a colourless, highly-refractive liquid, having a pungent odour, a density of 1.001 at 15° , and boiling at 160° – 161° . With free oxygen it combines energetically to phosphenylic acid, the action being attended with inflammation unless the liquid is cooled. It also unites directly with sulphur, forming phenylphosphine sulphide, $\text{C}^6\text{H}_5\text{PH}^2\text{S}$, a thick liquid, which on continued heating breaks up into isophosphophenyl sulphide (p. 1575), phenylphosphine, and hydrogen sulphide: $2\text{C}^6\text{H}_5\text{P}^2\text{SH}^2 = \text{C}^6\text{H}_5\text{PS} + \text{C}^6\text{H}_5\text{PH}^2 + \text{H}^2\text{S}$. The action of sulphur on phenyl phosphine likewise gives rise to a crystalline substance, insoluble in ether, which appears to be triphenyl sulphide, $(\text{C}^6\text{H}_5)_3\text{S}$; it melts at 138° , is also soluble in hot nitric acid, and does not separate on cooling.

Phenylphosphonium iodide, $\text{C}^6\text{H}_5\text{PH}^2\text{I}$, is produced by direct combination of phenylphosphine with dry hydrogen iodide. It forms white needles, which, by heating in an indifferent gas, or by contact with water, are resolved into hydriodic acid and phenylphosphine.

Phenylphosphine is but slightly soluble in concentrated hydrochloric acid, but the solution mixed with platinum chloride yields phenylphosphonium platinumchloride, $(\text{C}^6\text{H}_5\text{PH}^2\text{Cl})^2\text{PtCl}_4$.

Diethylphenylphosphine, $\text{C}^6\text{H}_5\text{P}(\text{C}^2\text{H}_5)^2$ (Michaelis a. Ananoff, *Ber.* viii. 493). The zinc-chloride of this base is formed by gradually adding phosphenyl dichloride to zinc-ethyl, both being diluted with benzene; and remains on removing the solvent by distillation as a viscous liquid which, when decomposed by sodium carbonate and then saturated with caustic potash, yields the free base in the form of an oily layer.

Diethylphenylphosphine is a colourless pungent liquid, boiling at 221.9° (corr.), and having a specific gravity of 0.9571 at 13° . It is but slowly oxidised in the air, but if heated in oxygen, it explodes and deposits carbon. Pure chlorine causes its ignition, but chlorine diluted with air converts it into the normal chloride, $\text{PCl}_3(\text{C}^2\text{H}_5)^2\text{Cl}^2$, and sulphur unites with it, forming the corresponding sulphide. Diethylphenylphosphine, though a distinctly characterised base, does not yield well-defined salts. With hydrochloric acid, it yields a solid monohydrochloride and a liquid dihydrochloride, both unstable and ill defined; platinum chloride added to the hydrochloric solution of the base throws down a crystalline yellow salt, containing $[\text{PCl}_3(\text{C}^2\text{H}_5)^2\text{HCl}]^2\text{PtCl}_4$.

Diethylphenylphosphine chloride, $(\text{C}^2\text{H}_5)^2\text{C}^6\text{H}_5\text{PCl}^2$, is produced as above indicated, and forms a thick oily liquid which fumes slightly in the air, and has a faint but not disagreeable odour. Heat decomposes it, with separation of carbon, but if strongly cooled, it becomes solid and crystalline; when dissolved in cold water, it yields an opalescent solution which becomes clear on heating.

Diethylphenylphosphine oxide, $(\text{C}^2\text{H}_5)^2\text{C}^6\text{H}_5\text{PO}$, is very slowly formed by direct oxidation, but can be readily prepared by evaporating an aqueous solution of the chloride and removing the last trace of hydrochloric acid by means of silver oxide. The crude oxide when distilled condenses to a crystalline solid, which has a fruity odour, is very soluble and deliquescent, melts at 55° – 56° , and boils above 360° .

Diethylphenylphosphine sulphide is a viscous substance, formed by the direct combination of the base with sulphur. It is almost insoluble in water, has an unpleasant smell, solidifies in a freezing mixture, and boils above 360° .

Triethylphenylphosphonium iodide, $(\text{C}^2\text{H}_5)^3\text{C}^6\text{H}_5\text{PI}$, is produced by the direct union of diethylphenylphosphine and ethyl iodide, and forms white needles which melt at

115°, and are not decomposed by aqueous potash, but silver oxide acts on it, with production of the hydroxide, a white crystalline alkali, capable of precipitating aluminium or copper salts. The *platinochloride*, $[\text{Pt}^{\text{H}}(\text{C}^{\text{H}}^3)^3\text{Cl}]^2 + \text{PtCl}_4$, crystallises in orange-yellow leaflets, melting below 100°.

Methyl-diethylphenylphosphonium iodide, $(\text{CH}_3)(\text{C}^{\text{H}}^3)^2\text{C}^{\text{H}}^3\text{PI}$, prepared in the same manner as the corresponding triethyl-compound, methyl iodide being used in the place of ethyl iodide, forms snow-white crystals, which melt at 95°. The *hydroxide* and *platinum salt* resemble those of the ethyl-base.

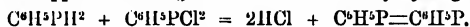
Dimethylphenylphosphine, $(\text{CH}_3)_2\text{PC}^{\text{H}}^3$, prepared like the diethyl compound, forms a colourless, highly refracting liquid, insoluble in water, boiling at 192° (corr.), and having a specific gravity of 0.9768 at 11°. It has a much more powerful odour than the diethyl-base; oxidises quickly in the air; and forms a solid mono- and a liquid di-hydrochloride.

The iodides, hydroxides, and platinochlorides of ethyldimethylphenylphosphonium and trimethylphenylphosphonium have likewise been prepared.

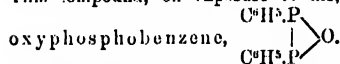
PHOSPHINIC ACIDS. These acids, represented by the formulæ PH^2RO^3 and PHR^2O^3 , or $\text{PO}(\text{OH})^2\text{R}$ and $\text{PO}(\text{OH})\text{R}^2$, R denoting a monatomic alcohol-radicle, are formed from the primary and secondary phosphines by fixation of 3 and 2 atoms of oxygen, and may be regarded as orthophosphoric acid, $\text{PO}(\text{OH})^3$, in which one or two of the OH-groups is replaced by an alcohol-radicle. The phosphinic acids of the fatty series have already been described (vii. 956); also phenylphosphinic acid, $\text{PO}(\text{OH})^2\text{C}^{\text{H}}^3$, at p. 1576 of this volume under the name of *phosphenylic acid*.

Diphosphophosphinic acid, $\text{PO}(\text{OH})(\text{C}^{\text{H}}^3)^2$, is formed by heating 1 mol. phosphonyl dichloride with 2 mols. mercury-diphenyl and benzene to 160°. It dissolves in boiling hydrochloric acid, and crystallises from boiling nitric acid in long needles. It is insoluble in water, slightly soluble in cold alcohol, and melts at 174°. Its silver salt crystallises in white silky needles (Michaelis a. Graff, *Ber.* viii. 922, 1304).

PHOSPHOBENZENE, or DIPHOSPHENYL, $\text{Cl}^2\text{H}^{10}\text{P}^2 = \text{C}^6\text{H}^5\text{.P}=\text{P.C}^6\text{H}^5$, is prepared by adding phosphonyl dichloride (16 gr.) in drops to phenylphosphine (20 gr.) in a reflux apparatus through which a stream of dry hydrogen is passed:



At the end of the reaction, which must be assisted by gentle heating to remove the last traces of hydrochloric acid, a residue is obtained consisting of diphosphenyl in the form of a yellowish powder insoluble in hot water, also in alcohol and in ether. This compound, on exposure to air, is oxidised to diphosphenyl oxide, or



By oxidation with *nitric acid* it is converted into phosphenyloxy or phosphenylic acid. *Chlorine* acts violently on phosphobenzene, producing inflammation; when diluted with carbon dioxide it acts more regularly, forming phosphonyl dichloride; oxyphosphobenzene similarly treated yields the dichloride and oxychloride of phosphonyl. *Hydrochloric acid* converts phosphobenzene into phenylphosphine and phosphenyloxy acid. *Strong sulphuric acid* decomposes it, with evolution of sulphur dioxide; dilute sulphuric acid and alkalis do not act upon it.

PHOSPHOMOLYBDATES. See MOLYBDENUM (p. 1335).

PHOSPHORITE. See PHOSPHATES (p. 1597).

PHOSPHORUS. *Occurrence in Ancient Iron.*—A scoria produced in Roman or Etruscan times from the specular iron ore of Elba, was found to contain 0.34 per cent. P^2O^3 , which is about eight times as great as the proportion in the natural ore, usually 0.04 per cent. A piece of metallic iron from the same district gave 0.096 per cent. P; other specimens from 1.08 to 1.10 per cent. (A. E. Arnold, *Chem. News*, xl. 138). On the proportion of phosphorus in Belgian iron ores and in the pig-iron and malleable iron prepared therefrom, see p. 1111.

Determinations of the Specific Gravities and Expansion-coefficients of phosphorus in the solid and liquid states have been made by Pisati a. De Franchis (p. 935). According to the same authorities phosphorus melts at 44.4°–44.5°, and boils under 762 mm. at 278.3°.

On the *Phosphorescence* of phosphorus, see Jonbert (*Compt. rend.* lxxviii. 1853).

Crystals of Phosphorus.—W. D. Hermann (*Ber.* vi. 1415) has obtained crystals of phosphorus by placing a piece of phosphorus at one end of a tube, exhausting the air with a Sprengel pump, then melting the phosphorus, and keeping it in the dark. After a few hours, a row of shining points becomes visible, and these in two or three days

grow to distinct crystals, attaining in a month or six weeks a diameter of 3 to 5 mm. They are colourless and transparent, with diamond lustre and great refracting power, but become yellow and opaque on exposure to light. According to Maskelyne's measurements, they exhibit the faces of the cube, octohedron, dodecahedron, tetrakis-hexahedron, triakis-octohedron, and ikositetrahedron.

Red phosphorus may be obtained in the crystalline state by heating ordinary phosphorus nearly to the softening point of difficultly fusible glass (about 503°). The allotropic phosphorus thus obtained had in the compact state the aspect of a violet-black fused body, with conchoidal fracture and translucent edges, and the crystals were found in cavities of this mass (Troost & Hautefeuille, *Compt. rend.* lxxvi. 1175). The same authors also find (*ibid.* lxxviii. 748) that the density and heat of combustion of red phosphorus vary continuously according to the temperature at which it has been prepared, and it is only in the crystallised state, obtained as above, that red phosphorus exhibits the characters of a definite chemical species. Its density in this state is 2.34 at 0°, and 1 gram in burning evolves 5272 gram-degrees of heat. Phosphorus prepared by heating for 650 hours in an oil-bath at 265° has a density of 2.148 at 0°, and 1 gram in burning gives out 320 heat-units more than crystallised red phosphorus; ordinary red phosphorus gives out 580 units more; the product obtained at 360° has a density of 2.19, and gives out 290 units more; that prepared at 500° has a density of 2.293 and likewise a greater heat of combustion, whereas the heat of combustion of the fused product obtained at 180° is less by 50 units than that of crystallised red phosphorus. Hittorf, by heating red phosphorus to 530° in a vacuum tube and allowing the vapour to condense in the upper part heated only to 447°, obtained it in red crystals which he describes as rhombohedrons approaching very nearly to the cube (vi. 933).

The phenomena attending the conversion of ordinary into red phosphorus are analogous to those observed in the conversion of liquid cyanic acid into cyanilide (vi. 518). The vapour of the phosphorus first acquires the maximum tension corresponding with the temperature at which the change takes place; and this tension gradually diminishes during the formation of the red phosphorus, till it attains a certain value representing the transformation-tension at the same temperature. The following table shows the two tensions observed at different temperatures:

Temperature	Maximum-tension	Transformation-tension
360	3.2	0.12 atm.
440	7.5	1.75
487	—	6.80
494	18.0	—
503	21.9	—
510	—	10.8
511	26.2	—
531	—	16.0
550	—	31.0
577	—	56.0

The black phosphorus, obtained, according to Blondlot (iv. 503), by sudden cooling of melted phosphorus, previously distilled in a stream of hydrogen, is, according to E. Ritter (*Compt. rend.* lxxviii. 192), a mixture of phosphorus with phosphide of arsenic. From pure phosphorus Ritter was unable to obtain a black modification; but after fusion under a solution of arsenious or arsenic acid, and remaining for some time in contact with the solution, it became black; and on treating it with carbon sulphide, the pure phosphorus dissolved out, and phosphide of arsenic was left in the form of a shining black powder having nearly the composition As_2P .

Reactions. Detection. Estimation.—Pure phosphorus precipitates gold, copper, and palladium from solutions of their salts in the metallic state; silver as phosphide; whereas platinum, uranium, nickel, iron, zinc, cadmium, and cobalt are not precipitated by phosphorus (Böttger, *Chem. Centr.* 1878, 208; compare iv. 506).

On the detection and estimation of Phosphorus in Iron and Steel, see IRON (p. 1102).

For the detection and separation of phosphorus in *Food-residues*, and other fatty substances, A. von Bastelaer proposes a method depending on the solubility of phosphorus in ether, and its complete indifference to a strong solution of ammonia. The substance to be tested, after being mixed with water to a thin paste, is briskly agitated several times with ether; the ether is left to evaporate at the ordinary temperature in a shallow dish; and the residue is carefully treated with warm water at 50°–60°, whereupon the phosphorus, with part of the fat, collects together under the water, to a liquid spherical mass from which the fat may be dissolved out by strong aqueous ammonia (*N. Jahrb. Pharm.* xl. 24; *Pharm. J. Trans.* [3], iv. 322).

Detection and Estimation of Phosphoric Acid.—Small quantities of free phosphoric acid in solution may be detected by introducing a ring of platinum wire, wetted with the liquid, into a colourless hydrogen-flame close to the end of the efflux-tube, whereupon, if phosphorus is present, the flame immediately becomes green. The presence of soda interferes with the reaction; if metallic or earthy-alkaline phosphates are present, it may be developed by moistening the loop of wire with sulphuric acid (F. Selmi, *Gazz. chim. ital.* 1876, 34).

The following method of detecting and estimating phosphoric acid by the blow-pipe, depending on the opalescence imparted to a borax-bead by a certain quantity of phosphoric acid, is described by A. W. Ross (*Chem. News*, xxxii, 217). This opalescence is directly produced by the phosphates of the alkali-metals and heavy metals, also by cast-iron, many tourmalines, axinite, and similar minerals. Its strength may be determined by comparison with a bead of the same size, to which the same degree of opalescence has been imparted by a standard solution of phosphoric acid. The phosphates of the alkaline earths form white beads like snow-balls; those of the earths form amorphous fragments which float in the transparent borax-bead. To set free the phosphoric acid from these compounds, and develop the opalescence, the borax-bead is fused with about a third of its volume of magnesium sulphate, and the white opaque bead thus produced is made clear again by cautious addition of a small quantity of potassium carbonate. If now into a bead thus prepared there be introduced the smallest quantity of a phosphate, it will be decomposed on heating, and as the bead cools, the characteristic opalescence will appear, and may be compared with that of a standard bead prepared in a similar manner.

Estimation as Ammonio-magnesium Phosphate.—The degree of accuracy attainable by this method has been carefully investigated by T. R. Ogilvie (*Chem. News*, xxxi, 274; xxxii, 5, 12, 70). The experiments were made on a quantity of hydro-disodic phosphate containing 0.2021 gram P_2O_5 , with a magnesia mixture containing in 1 c.c. 0.0613 gram $MgCl_2$, 0.1401 gram NH_4Cl , and 0.0191 gram NH_3 , the same excess of free ammonia being present in each experiment. The volume of solution was in every case about 100 c.c., and the time allowed for precipitation six hours. When the excess of magnesia used did not exceed 58 per cent. of that required, the results were absolutely correct; with a large excess of magnesia the results became rather excessive. When sulphate of magnesium was substituted for the chloride, accurate results were obtained with an excess of 13 per cent., but with 58 per cent. and upwards they became too high. Chloride of ammonium, up to 2.5 grams, diminished but very slightly the weight of precipitates obtained with an excess of 13 and 58 per cent. of magnesia. Sulphate of ammonium, up to 0.5 gram, had no effect with an excess of 58 per cent. magnesia. Oxalate and citrate of ammonium, or mixtures of the two, considerably diminished the precipitate when a small excess of magnesia was present, but with a large excess of magnesia the results were much too high. There is thus for every proportion of oxalate and citrate a proportion of magnesia which will give an accurate result by a balance of errors. When the solution contained 0.035 gram ferric oxide, 0.013 gram alumina, 0.5 gram ammonia, and 1 gram of citric acid, the results with an excess of 58 per cent. and upwards of magnesia were rather too high. With the quantities of ferric oxide, alumina, and citric acid doubled, the results with the same magnesia were distinctly too low. The citric acid in both cases was sufficient to yield a precipitate free from iron. When the alumina was increased to 0.26 gram, and the citric acid to 4 grams, the results became very low. In the last two cases an increase in the proportion of magnesia did not increase the precipitate. The removal of the mother-liquor, and the solution and reprecipitation of the ammonio-magnesian phosphate, is attended with loss if the original precipitate is pure, but if it contains an excess of magnesia the result may be correct, the excess of magnesia hindering the solvent action of the ammonium salts. Precipitation at the boiling heat gives accurate results with pure solutions and a small excess of magnesia, but with a large excess of magnesia the results are higher than in the cold. In presence of ammonium oxalate and the other salts mentioned above, the results obtained at boiling heat are more irregular, and generally higher than in the cold.

The general conclusion drawn from these experiments is that the opposite errors due to the solubility of ammonio-magnesium phosphate in oxalate and citrate of ammonium, and to the precipitation of basic salts in presence of excess of magnesia, are the cause of a wide range of results in commercial analyses, and that accuracy can be obtained only when the phosphoric acid exists as an alkaline salt, or is brought into this condition by the molybdic method.

In a paper read by E. M. Dixon, before the Philosophical Society of Glasgow, January 18, 1875, it is shown that the presence of large quantities of sodium or ammonium sulphate increases the weight of the ammonio-magnesian phosphate. Also

that oxalate and citrate of ammonium retard precipitation; that, in the case of the oxalate, precipitation is complete in twenty-four hours: but that with a large proportion of citrate, and a small excess of magnesia, precipitation is incomplete even then. As the solvent action of the oxalate is certainly, and that of the citrate probably, removable by the use of excess of magnesia and long standing, Dixon suggests such a procedure as the first stage of the determination, the impure precipitate to be finally redissolved and reprecipitated, in presence of a very small excess of magnesia.

J. Hughes (*Chem. News*, xxxi. 209) observes that the magnesia-method, when applied to the analyses of native phosphates, is apt to give results in excess, unless the original hydrochloric acid solution of the mineral has been previously evaporated to dryness, as in the contrary case the ammonia-magnesium phosphate may become mixed with more or less magnesium silicate.

As Phosphomolybdate.—O. Hehner (*Analyst*, 1879, 23) gives a review of all that has been previously contributed towards the estimation of phosphoric acid, either directly as phospho-molybdate, or indirectly by dissolving this precipitate in ammonia, precipitating with magnesia mixture, and weighing as magnesium pyrophosphate. The objection to weighing the dried phospho-molybdate precipitate is that it is found to contain percentages of phosphoric anhydride varying from 3.14 to 3.90. The explanation given by Lipowitz, that this variation is due to MoO_3 accompanying the precipitate in varying proportions, is confirmed by Hehner, who also finds that the quantity of MoO_3 precipitated increases with the temperature at which the precipitation took place. Hence low temperatures (30° – 35° C.) should be employed. The molybdic solution is best prepared according to the directions of Fresenius, by dissolving 1 pt. of molybdic acid in 4 pts. of ammonia of 0.96 sp. gr., and pouring this solution slowly into 15 pts. of nitric acid of 1.2 sp. gr., avoiding all rise of temperature. When the precipitate was thrown down by means of the above molybdate solution in a solution previously nearly neutralised by addition of ammonia, and at a low temperature, it was found to be free from molybdic acid. It was soluble in 21,186 pts. of water, in 8,117 of strong alcohol, and in 13,513 of dilute alcohol: hence this precipitate may be washed with dilute alcohol without sensible loss, and this liquid is to be preferred to water, because it does not cause the precipitate to pass through a good filter. Direct experiment showed that no one of these three liquids dissolved the precipitate sensibly when used for washing.

To obtain the precipitate in a form suited for weighing, the phosphate is precipitated with the precautions already mentioned, avoiding too great concentration of the solution, which encourages the simultaneous precipitation of molybdic acid. This precipitate is washed with dilute alcohol, leaving as much of the precipitate as possible in the beaker, the precipitate is dissolved from the beaker and filter by ammonia solution, and this solution is evaporated to dryness on the water-bath, the evaporation being several times repeated after the successive addition of small quantities of water. The precipitate then consists of ammonium phosphate and acid ammonium molybdate. It may be dried at 100° and weighed, a constant weight being quickly obtained, since all the ammonia which ordinarily escapes during the drying process has been removed by the repeated evaporations. The weight of this precipitate divided by 28.5 gives the weight of the phosphoric anhydride present. Comparative results obtained by this method and by weighing as magnesium pyrophosphate were closely concordant. The precipitation requires only two or three hours, and the estimation may be easily completed in a day. The molybdic acid may be recovered from the residues by acidifying with nitric acid, adding sodium phosphate, dissolving the precipitate formed on heating in ammonia, precipitating the phosphate with magnesia mixture, and the molybdic acid from the filtrate by nitric acid. The molybdic acid is then filtered, washed, and dried.

See also Finkener (*Ber.* x. 1638; *Chem. Soc. J.* xxxvi. 275).

According to R. W. Atkinson (*Chem. News*, xxxv. 127), silica, if present, must be separated previous to the precipitation of phosphoric acid by ammonium molybdate; according to E. H. Jenkins, on the other hand (*Sill. Am. J.* [3], xi. 204), the presence of silica does not interfere with the result.

O. Kerschalt (*Dingl. pol. J.* cccxxv. 158) precipitates phosphoric acid with a solution of *potassium molybdate* prepared by dissolving 1 pt. MoO_3 in 2 pts. KHO in 12 pts. hot water, mixing the cooled liquid with a solution of 1 pt. tartaric acid in 4 pts. water and with 15 pts. nitric acid, then boiling and filtering. The precipitate of potassium phospho-molybdate dried at 126° contains 3.956 per cent. P_2O_5 .

As Uranic Phosphate (iv. 514).—According to A. Kitchin (*Chem. News*, xxvii. 199), this salt is least soluble and is precipitated most quickly when the solution contains a sufficient quantity of ammonium acetate, and only a slight excess of acetic acid. After washing, drying, and ignition, the precipitate should be repeatedly

moistened with nitric acid and re-ignited till its colour is no longer green, but pure yellow. Its composition is represented most nearly by the formula $U^2P^2O^{11}$ or $2UO^3.P^2O^5$ [$U = 240$].

Bolohoubek (*Böhm. Ges. Ber.* 1876, Heft. 4), after precipitating the phosphoric acid with uranic acid, reduces the precipitate to uranous phosphate, determines the quantity of uranium in the resulting acid solution by means of a standard solution of permanganate, and thence deduces the amount of phosphoric acid present.

As Bismuth Phosphate.—E. Dransard (*Amer. Chem.* vi. 401) recommends a modification of Chancel's method (iv. 543), which consists in carefully neutralising the acid solution with sodium carbonate before adding the bismuth nitrate, and fusing the dried precipitate of bismuth phosphate and other basic bismuth salts with sodium carbonate in a small porcelain crucible, whereby sodium phosphate and metallic bismuth are formed. The sodium phosphate is dissolved out by water, the solution acidulated, and the phosphoric acid precipitated by ammoniacal solution of calcium chloride as calcium phosphate, which is then treated in the usual way.

Volumetric Methods.—An acidimetric method for the estimation of phosphoric acid and the quantity of alkali which must be added to a mixture of soluble alkaline phosphates to bring it up to trisodic phosphate, Na^3PO^4 , is described by Maly a. Hinterberger (*Zeitschr. anal. Chem.* 1876, 417). The solution is first made alkaline with excess of soda-ley, so as to ensure the formation of trisodic phosphate, and barium chloride is then added, whereby the whole of the phosphoric acid is precipitated as barium phosphate, and it only remains to determine the excess of alkali added by back titration, which may be done with normal hydrochloric acid, using corallin as indicator. The liquid must be kept hot, but it is not necessary to remove the barium phosphate by filtration. The method is especially applicable to free phosphoric acid and alkaline phosphates, but the solution must not contain any salts of the heavy metals.

J. Macagno (*Gazz. chim. ital.* 1874, 567) estimates phosphoric acid volumetrically by precipitating it as ammonium phosphomolybdate, reducing the molybdic acid therein contained to Mo^2O^3 with zinc and sulphuric acid, and reoxidising this oxide after removal of the zinc with a standard solution of permanganate.

A modification of Liebig's volumetric method of estimating phosphoric acid, viz. precipitation in acetic acid solution with a standard solution of ferric chloride, with potassium ferrocyanide as indicator, has been proposed by W. Stoddart (*Amer. Chem.* v. 235), consisting in the substitution of *thiocyanate* for the ferrocyanide, whereby the recognition of the end-reaction is greatly facilitated.

Comparison of various Methods.—M. Joulin (*Chem. News*, xxvii. 228, 309, 314) has made comparative experiments on the various methods in use for the estimation of phosphoric acid, from which he draws the following conclusions. The precipitation of phosphoric acid by *ammonia and a magnesium salt*, in presence of an excess of ammonium citrate, affords an excellent method of separating phosphoric acid from the bases usually associated with it, but the results obtained by direct weighing of the precipitate are too high. The separation of phosphoric acid by *uranic nitrate* from a solution slightly acidulated with acetic acid, gives results which are too low, if lime, ferric oxide, or alumina is likewise present. The most exact results are obtained by precipitating the phosphoric acid with a solution containing 400 grams citric acid and 20 g. magnesium carbonate in 200 litres of water mixed with 500 c.c. ammonia of 22° B. This liquid is to be diluted with water to 1 litre. In the resulting precipitate the phosphoric acid is estimated by titration with uranium solution.

Experiments on the relative accuracy of various methods of estimating phosphoric acid have also been made by Abesser, Jani a. Märcker (*Zeitschr. anal. Chem.* 1873, 239; *Chem. Soc. J.* xxvii. 387), who find that in the precipitation with *magnesia-mixture*, exact results are obtained only when this mixture is prepared with chloride instead of sulphate of magnesium, as in the latter case, the precipitate is always mixed with a certain quantity of basic magnesium sulphate which, if not compensated by the solubility of the ammonio-magnesium phosphate, is likely to make the results too high. With regard to the time required for complete precipitation of the phosphoric acid, they find that with a solution containing 0.1 to 0.15 g. phosphoric acid in 110 c.c. three or four hours standing is quite sufficient. For the separation of phosphoric acid from the alkaline earths or heavy metals, they recommend precipitation with ammonium molybdate, the digestion being continued from four to six hours.

Among volumetric methods of estimating phosphoric acid, Abesser, Jani a. Märcker have especially examined the uranium method and the results yielded by it with acid calcium phosphates, which, as a rule, they find to be lower than those obtained by gravimetric methods.

Fresenius, Neubauer, and Luck (*Zeitschr. f. anal. Chem.* x. 138) found that from a warm acetic acid solution of calcium phosphate, especially if the solution be too concentrated, calcium phosphate may separate as such, and thus escape titration with uranium acetate; and they proposed to modify the reaction so as to add the phosphatic solution to a measured quantity of uranium solution as long as potassium ferrocyanide gives a reaction (vii. 969). Abesser, Jani a. Märcker used solutions of phosphates in cold acetic acid, and applied heat only when nearly the whole of the phosphoric acid had been precipitated by the uranium acetate. They found, however, that the quantity of P_2O_5 in aqueous extracts from superphosphates, when determined gravimetrically by means of magnesium chloride mixture, differed on an average by + 29 per cent. from that obtained by a uranium solution titrated with a solution of sodium phosphate. On examining the latter precipitate for lime, after separating the phosphoric acid by Reissig's method, and the uranium by means of ammonium sulphide, 4.15 per cent. of CaO were found. Hence they inferred that the strength of the uranium solution used in estimating phosphoric acid in superphosphates should be determined by a solution of the latter instead of by sodium phosphate. For this purpose they employ tricalcic phosphate free from neutral phosphate and other admixtures, dissolved in the least possible excess of nitric acid, the strength of the solution being determined as above, by evaporation and ignition and weighing of the residual tricalcic phosphate. They further observe that in presence of ammonia salts, the titration of the phosphoric acid may come out somewhat too low, but that this error may be avoided by using a solution of uranic acetate instead of nitrate, or by titrating the solution of uranium nitrate with calcium phosphate, with addition of ammonium salts. Solutions of uranic acetate containing excess of acetic acid are not altered by light.

For the estimation of 'soluble' phosphoric acid—in case the process of washing out is found to be too tedious, and recourse must be had to digestion—it is recommended that the time of digestion be shortened as much as possible, in order to avoid increase or diminution of the quantity of soluble phosphoric acid during the process.

Separation of Phosphoric Acid from Ferric Oxide and Alumina.—The various methods proposed for the separation of phosphoric acid from these bases have been subjected to comparative examination by W. Flight (*Chem. Soc. J.* xxviii. 592) with the following results: The method of separating phosphoric acid from alumina by means of *silica* or *potassium silicate*, proposed by Berzelius and by Fuchs (iv. 548), not only presents great difficulties, but gives results which are too low. That of Otto, which consists in precipitating with *magnesia-mixture* while the alumina and ferric oxide are held in solution by *tartaric acid* (iv. 547), is likewise inexact, because the precipitated ammonio-magnesium phosphate is apt to get mixed with a magnesium salt of the organic acid; and further, as shown by Knapp (*Zeitschr. anal. Chem.* iv. 151), and confirmed by Pribram (*ibid.* v. 208), because the ammonio-magnesium phosphate is soluble in excess of tartaric acid, especially when alumina is present. The method is not improved by the substitution of citric for tartaric acid. Wackenroder's method of digesting the hydrochloric acid solution of ammonia and phosphoric acid with *barium carbonate* and then with *potash-ley* (*Arch. Pharm.* [2], lvii. 17), also gives inexact results, inasmuch as the phosphoric acid is not wholly carried down in the baryta-precipitate. The *molybdic acid method*, as proposed by Sonnenschein (iv. 546) and modified by Ogilvie (p. 1583), yields sufficiently accurate results, but it requires a nitric acid solution, which is not always available. Rose's method of separating phosphoric acid from ferric oxide by fusion with an *alkaline carbonate* always yields an iron oxide still retaining phosphoric acid. Reynoso's method, modified by Reissig, of precipitating the phosphoric acid as *stannic phosphate*, cannot be used in presence of large quantities of iron oxide or alumina; it is, moreover, affected with an error arising from the contamination of commercial tin with arsenic. Rose's method with *mercurous nitrate* (iv. 543) is likewise defective on account of the difficulty, already pointed out by Schweizer (*Ber.* iii. 310), of completely expelling the nitric acid by evaporation, and even as modified by Munroe (vii. 967), it is not applicable to the separation of phosphoric acid from ferric oxide. The method of precipitating the phosphoric acid and ferric oxide together by ammonia, and digesting the precipitate with *ammonium sulphide*, requires, according to Schweizer, a repetition of the treatment, and even then does not yield exact results. The *bismuth-method* (p. 1585) is likewise inapplicable; that of Chancel, which consists in precipitating the phosphoric acid with *nitrate*, or better with *carbonate of silver*, is also inexact in presence of iron oxide or alumina, inasmuch as these oxides are precipitated at the same time, and the silver phosphate cannot be completely dissolved out from the precipitate by ammonia.

The following is, according to Flight's experiments, the best method of separating phosphoric acid from ferric oxide and alumina: (1). From Ferric oxide. The

slightly acid solution is completely reduced by a stream of hydrogen sulphide, then treated with excess of ammonium sulphide, heated nearly to boiling, filtered, and the precipitate is washed with water containing hydrogen sulphide. The whole of the phosphoric acid is then found in the filtrate. (2). From Alumina. The solution of the aluminium phosphate is mixed with an excess of caustic soda sufficient to keep the whole of the alumina in solution, and then treated with a quantity of barium chloride sufficient to throw down all the phosphoric acid in the form of barium salt. The liquid is left at rest for some hours, and protected from access of carbonic acid, then filtered, and the precipitate is washed with water containing soda, the addition of which is necessary, as the barium phosphate would be decomposed by pure water, and the estimation of the phosphoric acid would then come out much too low. (3). From Ferric Oxide and Alumina together. The solution, not too acid, is mixed, according to Chancel's method (i. 154), with excess of sodium thiosulphate, boiled for some time, and filtered, whereupon the whole of the iron remains in solution, together with part of the phosphoric acid, whilst the alumina is precipitated together with the rest of the phosphoric acid. The separation may then be effected by the methods (1) and (2) above described. If the phosphoric acid is not in excess with respect to the alumina, the whole of it will be found in the precipitate, and the iron-solution will be free from it.

The precipitates formed by excess of phosphoric acid in ferric and aluminic solutions are represented by the formulæ $7Al_2O_3 \cdot 6P_2O_5$ and $7Fe_2O_3 \cdot 6P_2O_5$.

H. Pellet (*Bull. Soc. Chim.* [2], xxvii. 106) estimates phosphoric acid, alumina, and ferric oxide when they occur together in solution as follows: 1. The solution is mixed with excess of ammonia and calcium chloride, whereby a precipitate is formed consisting of alumina, ferric oxide, and calcium phosphate. This precipitate is ignited and weighed; the residuo is dissolved in hydrochloric acid; the phosphoric acid is determined in one portion of the solution with uranium; the ferric oxide in another by stannous chloride; and the alumina is estimated by difference.

F. Jean (*Compt. rend.* lxxviii. 1305) estimates phosphoric acid, in presence of lime, iron oxide, alumina, &c., by dissolving the phosphate under examination in strong nitric acid, mixing the filtered solution with a slight excess of ammonia, redissolving the precipitate in acetic acid, and precipitating the phosphoric acid with uranium acetate. The resulting precipitate after washing, drying, and ignition contains 20.05 per cent. P_2O_5 .

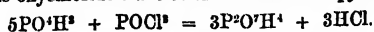
A. Classen separates phosphoric acid from certain bases by precipitation with *potassium oxalate*. This method is applicable to salts whose bases, like calcium, are at once completely precipitated by soluble oxalates; also to salts of manganese, zinc, cobalt, and nickel, the metals of which are precipitated as double oxalates easily decomposed by excess of acetic acid, which dissolves the alkaline oxalate and completely precipitates the oxalate of the heavy metal. For the details of this method, see *Zeitschr. anal. Chem.* 1879, 189, 373; *Chem. Soc. J.* 1879, xxxvi. 979 and 1054-1056.

B. W. Gerland (*Chem. News*, xxxiii. 133) modifies the oxalic acid method commonly used in the analysis of phosphorites on the ground that the presence of oxalic acid hinders the precipitation of ferric and aluminic phosphates by means of alkaline acetates. The weighed sample of phosphorite is dissolved in nitric or hydrochloric acid; the liquid, neutralised as nearly as possible without formation of a permanent precipitate, is boiled, and mixed with a slight excess of an oxalate; acetate of sodium or ammonium is then added; and the liquid is removed from the source of heat. On cooling, the whole of the lime separates as an oxalate in the form of a heavy powder. The iron and aluminium are best removed from the filtrate by precipitation with ammonium sulphide at a gentle heat. The precipitate consists of iron sulphide and aluminium phosphate, together with silica, which obstinately adheres to it. The determination of the phosphoric acid in it is effected by the molybdic method.

Haloid Compounds of Phosphorus.

Chlorides. An elaborate investigation of the action of these compounds on the acids of phosphorus has been made by A. Gauthier (*J. pr. Chem.* [2], viii. 350).

1. *Action of Phosphorus Oxychloride on Orthophosphoric Acid.*—When these substances are mixed in accordance with the equation, $2PO_4H^3 + POCl^3 = 3PO_3H + 3ClH$, no apparent change is produced until the mixture is heated on the water-bath, the reaction then taking place in the manner just indicated. The use of a smaller proportion of phosphorus oxychloride leads to the formation of pyrophosphoric acid:



Pyrophosphoric acid is however produced when metaphosphoric acid and orthophos-

Trichloride, PCl_3 .—*Ira Remsen (Sill. Am. J. [3], xi. 365)* finds that this compound is easily converted into POCl_3 by the action of ozone, and regards this reaction as affording an additional proof of the quinquivalence of phosphorus.

According to *Michaelis (Ber. viii. 504)*, when phosphorus trichloride in small quantities is added without cooling to water at ordinary temperatures, the liquid at first remains perfectly clear, but as soon as a certain quantity of the trichloride has been decomposed, and the temperature has consequently risen, the liquid becomes turbid, and a small quantity of phosphorus separates out. When, on the contrary, the trichloride is dropt into boiling water, not a trace of phosphorus separates out. Ice-cold water, into which phosphorus trichloride is dropt, also remains clear, but becomes turbid and deposits a small quantity of phosphorus when heated. According to *Geuther*, on the other hand (*Jenaische Zeitschrift [2], iii. 2nd Suppl. 116*), the precipitation observed by *Michaelis* takes place only when the phosphorus chloride contains arsenic, and the solid body thus separated is not phosphorus but arsenic.

The action of phosphorus chloride on *potassium thiocyanate* gives rise to the formation of a compound, $\text{C}^2\text{H}^{18}\text{N}^4\text{S}^4\text{O}$, which crystallises in white slender needles (*Lössner, J. pr. Chem. [2], vii. 474*).

Oxychloride, POCl_3 , and *Ethoxychloride*, $\text{PO}(\text{OC}^2\text{H}_5)\text{Cl}_2$.—On the reactions of these bodies with the acids and other compounds of phosphorus, see p. 1587-9.

Pentafluoride, PF_5 (*T. E. Thorpe, Liebig's Annalen, clxxxii. 201-205*).—When phosphorus pentachloride is gradually added to arsenic trifluoride (obtained by heating arsenic trioxide with fluorspar and sulphuric acid), a violent reaction takes place, resulting in the formation of arsenic trichloride and phosphorus pentafluoride, in accordance with the equation :



Phosphorus pentafluoride is a colourless gas, having a very pungent odour, and attacking the mucous membranes. It fumes in the air, and reacts with water forming phosphoric and hydrofluoric acids. Its density is 63.23, that of hydrogen being 1 (theory requires 63). Under the pressure of 12 atmospheres at 7° , it exhibits no marked deviation from Boyle's law.

The gas neither burns nor supports combustion. It is not affected by the passage of electric sparks through it, either when pure, or when mixed with hydrogen or oxygen. It combines with dry ammonia to form a yellowish-white solid body, represented by the formula $2\text{PF}_5 \cdot 5\text{NH}_3$. A solution of the gas in aqueous ammonia deposits, on evaporation, crystals of ammonium phosphate, $\text{H}_2(\text{NH}_4\text{P})\text{O}_4$, and ammonium and hydrogen fluoride, $\text{HF} \cdot \text{NH}_4\text{F}$.

ACIDS OF PHOSPHORUS.

The Melting Points, and the Heats of Fusion, Solution, and Formation of these acids, have been determined by *J. Thomsen (Ber. vii. 966)* with the following results:—

Heat of Fusion.

	Melting point	Heat of fusion
PO^4H^3	38.6°	2520 gram-degrees
PO^3H^3	70.1	7070
PO^2H^3	17.4	2400

Heat of Solution.

	Crystallised acid	Fused acid
$(\text{PO}^4\text{H}^3, \text{Aq})$	+ 2690 gram-degrees	5210 gram-degrees
$(\text{PO}^3\text{H}^3, \text{Aq})$	— 130	2940
$(\text{PO}^2\text{H}^3, \text{Aq})$	— 200	2200

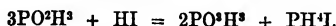
Heat of Formation.

Crystallised acid	$(\text{P}, \text{O}^4, \text{H}^3)$	302560 gram-degrees
	$(\text{P}, \text{O}^3, \text{H}^3)$	227680
	$(\text{P}, \text{O}^2, \text{H}^3)$	139950
Fused acid	$(\text{P}, \text{O}^4, \text{H}^3)$	300040
	$(\text{P}, \text{O}^3, \text{H}^3)$	224610
	$(\text{P}, \text{O}^2, \text{H}^3)$	137550
Aqueous solution	$(\text{P}, \text{O}^4, \text{H}^3, \text{Aq})$	305250
	$(\text{P}, \text{O}^3, \text{H}^3, \text{Aq})$	227550
	$(\text{P}, \text{O}^2, \text{H}^3, \text{Aq})$	139750

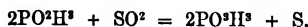
On the reactions of these acids with the Haloid compounds of Phosphorus, see pp. 1587-1589.

Hypophosphorous Acid, $\text{H}_3\text{PO}_2 = \text{HP}(\text{OH})_2$. On the crystallisation of this acid, see vii. 965. The barium salt, $\text{BaH}_2\text{P}_2\text{O}_4 + \text{H}_2\text{O}$, forms monoclinic crystals, having the axial ratio $a : b : c = 2.0017 : 1 : 1.5760$, and the angle $ac = 80^\circ 27'$ (Topsöe, *Wien. Akad. Ber.* 2 Abth. lxxix. 261). Compare Rammelsberg (*Chem. Soc. J.* 1873, 5). Sp. gr. 2.718 at 10° , and 2.891 at 17° ; of the *magnesium salt*, $\text{MgH}_2\text{P}_2\text{O}_4 + 6\text{H}_2\text{O}$, 1.5886 at 12.5° , and 1.5681 at 14.5° (C. A. Mohr, *Sill. Am. J.* [3], xiv. 281).

Reactions.—When perfectly dry *hydrogen iodide* is passed over hypophosphorous acid, a violent reaction takes place, accompanied by great rise of temperature. The products are phosphorous acid and phosphonium iodide :



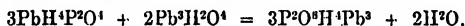
2. Dry *sulphur dioxide* reacts with hypophosphorous acid in the manner indicated by the equation :



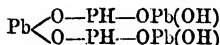
the chief products being phosphorous acid and free sulphur. At the same time, however, hydrogen sulphide is evolved, and some phosphoric acid is formed. The former of these bye-products is due, as found by direct experiment, to the action of free sulphur on hypophosphorous acid; the latter to the action of sulphur dioxide on phosphorous acid at high temperatures.

3. *Nascent hydrogen* does not act either on free hypophosphorous acid or on its alkaline salts (Ponndorf, *Jenaische Zeitschrift*, [2], iii. 2nd Suppl. p. 45).

By prolonged boiling of normal *lead hypophosphite* with lead hydrate, $3\text{PbO} \cdot \text{H}_2\text{O}$, a basic lead salt, $\text{P}^2\text{O}^3\text{H} \cdot \text{Pb}^2$, is obtained in the form of a homogeneous yellowish-grey powder made up of microscopic needle-shaped transparent crystals :

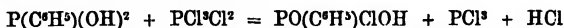


The constitution of this salt may be represented by the formula

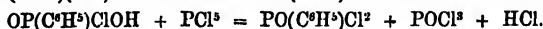


and affords further evidence of the correctness of the formula $\text{HP}(\text{OH})_2$ usually assigned to hypophosphorous acid, according to which it contains an atom of trivalent phosphorus associated with 1 at. hydrogen and two hydroxyl-groups (Ponndorf).

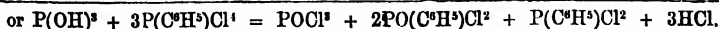
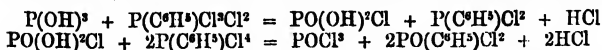
Phosphorous Acid, PII^3O^3 . Of the two constitutional formulæ by which this acid is represented, viz. $\text{P}'''(\text{OH})^3$ and $\text{OP}^2\text{H}(\text{OH})_2$, the first certainly affords the readiest explanation of the formation of the acid by the action of water on phosphorus trichloride, and of most of the reactions between the halogen-compounds and acids of phosphorus investigated by Geuther (p. 1588). On the other hand, Michaelis a. Ananoff infer, from the action of phosphorus pentachloride on phosphenyloous acid, and of phosphenyl tetrachloride on phosphorous acid, that the latter is correctly represented by the formula $\text{OPHI}(\text{OH})_2$ (p. 1578). Geuther, however, points out (*Jenaische Zeitschrift* [3], iii. 2nd Suppl. 116) that the former of these reactions, which gives rise to phosphenyl oxychloride, $\text{POCl}^2 \cdot \text{C}^6\text{H}^5$, together with POCl^3 , PCl^3 and HCl , may be satisfactorily explained on the hypothesis that phosphenyloous acid has the constitution $\text{P}(\text{C}^6\text{H}^5)(\text{OH})_2$, [analogous to $\text{P}(\text{OH})_3$], and that the phosphorus pentachloride acts like a mixture of PCl^4 and Cl^2 , thus :



and



A similar explanation is given by Geuther of the action of phosphenyl tetrachloride on phosphorous acid, based on the known fact that phosphenyl tetrachloride is resolved by heat into chlorine and the corresponding dichloride, thus :



It must be admitted, however, that the explanation of these reactions given by Michaelis a. Ananoff is more simple and direct.

Crystallised phosphorous acid may be prepared by heating the trichloride to 60° and passing the vapour by means of a current of dry air through two flasks each

containing about 100 grams of water cooled to 0° . In about four hours the contents of the first flask are found to be saturated with the phosphorous chloride and converted into a thick crystalline mass of phosphorous acid. The adhering liquid may then be drained off, and the crystals washed with small quantities of ice-cold water, and finally dried in a vacuum (Grosheintz, *Bull. Soc. Chim.* [2], xxvii. 433).

Metallic Phosphites. For the analysis of these salts, Kraut a. Precht (*Liebig's Annalen*, clxxvii. 274) recommend Rose's process, which consists in dissolving the phosphite in hydrochloric acid, adding an excess of pulverised mercuric chloride, and heating the mixture on a water-bath till the resulting mercurous chloride is completely deposited, collecting the deposit on a weighed filter, drying it at 100° , and weighing. If the filtrate be then freed by hydrogen sulphide from mercury and other bases which interfere with the determination of phosphoric acid, the amount of that acid produced may be estimated by precipitation with magnesia mixture, and a verification of the result thereby obtained.

Barium Phosphite, according to Kraut (*Lieb. Ann.* clxxvii. 274) and Rammelsberg (*Ber.* ix. 1577), has the composition BaHPO_3 , and not $\text{Ba}^2\text{H}^4\text{P}^2\text{O}_7$, formerly assigned to it (vi. 937). It is apt to retain small quantities of phosphate—acid phosphate, $\text{BaH}^4\text{P}^2\text{O}_7$, according to Rammelsberg—which may disguise its true composition. Rammelsberg also finds by new experiments that the barium salt, like other phosphites, gives off hydrogen, and leaves a residue of phosphide and pyrophosphate, a result which throws light on a long-established error respecting the composition of the phosphites of the alkaline-earths and of nickel as well as the abnormal results obtained in the analysis of the magnesium and zinc salts (vi. 937).

Trisodic Phosphite, PO^3Na^3 .—To obtain this salt, a concentrated solution of disodic phosphite, $\text{PO}^3\text{Na}^2\text{H}$, is first prepared by mixing pure phosphorous acid with sodium hydroxide to slight alkaline reaction, and to this solution is added a quantity of strong aqueous soda-solution equivalent to 4 mols. NaHO . The mass is then left to itself for two hours, after which strong alcohol is added, the supernatant alcoholic liquid is separated from a viscid syrup which settles down, and the latter, consisting of pure trisodic phosphite, is purified by repeatedly pouring strong alcohol upon it, and working it up therewith, and finally dried in a vacuum over sulphuric acid (C. Zimmermann, *Liebig's Annalen*, clxxv. 1).

Triethyl phosphite, $\text{PO}^3(\text{C}^2\text{H}_5)^3$.—This compound, which Railton obtained by the action of phosphorus trichloride on dry sodium ethylate (iv. 533), is prepared by Zimmermann as follows: The sodium ethylate, after being brought to a constant weight by heating it at 180° – 200° , is pulverised and mixed with ether free from alcohol and water; the mixture is well cooled; and the phosphorous chloride is added by drops with constant agitation. When the action is complete, the ethereal solution is decanted from the resulting sodium chloride, the ether is distilled off, and the remaining liquid is rectified at the heat of an oil-bath in a stream of hydrogen till it boils constantly at 188° .

Triethyl phosphite saponified with caustic potash is converted into phosphorous acid. By gradual oxidation with nitric acid it yields phosphoric together with oxalic acid. Heated in oxygen gas it is gradually oxidised to triethyl phosphate, $\text{PO}(\text{OC}^2\text{H}_5)^3$. This last reaction is effected by filling a small flask containing the phosphorous ether with oxygen, closing it, passing in a fresh portion of the gas after the first has been absorbed, and repeating this treatment several times. At a high temperature triethyl phosphite is resolved into phosphine, phosphoric acid, and probably ethylene. From these reactions Zimmermann infers that triethyl phosphite has the constitution $\text{P}(\text{OC}^2\text{H}_5)^3$, and not $\text{PO}(\text{C}^2\text{H}_5)(\text{OC}^2\text{H}_5)^2$, as in that case it should yield by saponification, not phosphorous acid, but ethyl-phosphinic acid, $\text{PO}(\text{C}^2\text{H}_5)(\text{OH})^2$.

Hypophosphoric Acid, $\text{H}^4\text{P}^2\text{O}^6 = (\text{HO})^2\text{OP} - \text{PO}(\text{OH})^2$ (T. Salzer, *Liebig's Annalen*, clxxxvii. 322; xciv. 28). This acid, intermediate in composition between phosphorous and metaphosphoric acids, is one of the constituents of the acid liquid (Pelletier's *acide phosphatique*) formed when phosphorus partially covered with water is exposed to the air (iv. 499). It may be separated in the form of a sparingly soluble sodium salt by treating the mixed acids with sodium carbonate or acetate.

Pure hypophosphoric acid is best obtained by treating the lead-salt suspended in water with hydrogen sulphide. Its aqueous solution is strongly acid, colourless, and inodorous, and may be boiled without decomposition, but when evaporated to a syrupy consistence, it is resolved by heat into phosphorous and phosphoric acids. In its behaviour with reagents, it is intermediate between phosphorous and phosphoric acids, which circumstance accounts for its having been so long overlooked in a mixture of these acids.

The acid is perfectly stable in aqueous solution, and is not affected by strong acids in the cold, but when boiled with dilute sulphuric or nitric acid, it is resolved, at a certain state of concentration, into phosphorous and phosphoric acids. The solution of the acid is not oxidised by dilute hydrogen peroxide when boiled therewith, and is not affected by potassium chromate, chlorine, or iodine, even at the boiling heat; neither does it reduce mercuric, auric, or platinic chloride. It produces in solutions of silver a white precipitate, which does not blacken on boiling. The solution is oxidised by potassium permanganate, slowly in the cold, and very rapidly when heated, being converted into phosphoric acid. It is not affected by hydrogen sulphide, sulphur trioxide, or nascent hydrogen.

Hypophosphoric acid is quadribasic. Its salts mostly react like those of hypophosphorous and phosphorous acids, but are much more stable. At high temperatures they give off hydrogen or phosphine, leaving a metallic phosphide or phosphate.

The *tetrasodic salt*, $\text{Na}_4(\text{PO}_3)_2 + 10\text{H}_2\text{O}$, obtained by gradually adding a solution of 1 pt. sodium carbonate to a solution of 1 pt. of the trisodic salt in 50 pts. water, separates in needle-shaped monoclinic crystals exhibiting the faces 0P , $2\text{P}\infty$, ∞P , $\frac{1}{2}\text{P}$. Cleavage parallel to $\infty\text{P}\infty$. Axes $a : b : c = 2.0435 : 1 : 1.9055$. Angle $ac = 35.55$. Twin-lamellæ according to the basal face are of somewhat frequent occurrence. The plane of the optic axes is the plane of symmetry: the acute bisectrix passes through the obtuse angle between 0P and $2\text{P}\infty$. The crystals dissolve in 50 times their weight of water. The cold saturated solution turns turmeric paper dark brown, and when mixed with a strong solution of sodium carbonate, deposits the normal salt unaltered.

Trisodiohydric Hypophosphate, $\text{Na}_3\text{H}(\text{PO}_3)_2 + 9\text{H}_2\text{O}$, is obtained by acting with less than one part by weight of crystallised sodium carbonate on one part of the acid sodium hypophosphate in solution. Its solution has an alkaline reaction. It loses its water of crystallisation at 100° , and at higher temperatures suddenly takes fire, and burns with a steady flame, giving off phosphoretted hydrogen gas, and leaving a white enamel. The crystals are monoclinic and have a strong vitreous lustre. Combination 0P . — P , 6P , 3P . — $6\text{P}\infty$. $\infty\text{P}\infty$. $4\text{P}\infty$. $5\text{P}\infty$. $20\text{P}\infty$. $4\text{P}\infty$. $6\text{P}\infty$; mostly tabular through predominance of 0P , sometimes also elongated in the direction of the orthodiagonal, and in that case broadly wedge-shaped, from predominant development of the lower face 0P and the front face $-6\text{P}\infty$. Some crystals exhibit twin-formation parallel to a face normal to the clinodiagonal, the crystals having then a rhombic habit. Axes $a : b : c = 1.5788 : 1 : 0.4348$, Angle $ac = 60^\circ 43'$. The plane of the optic axes is perpendicular to the plane of symmetry, acute bisectrix nearly perpendicular to 0P . Axial angle large.

Disodio-dihydric Hypophosphate, $\text{Na}_2\text{H}_2(\text{PO}_3)_2 + 3\text{H}_2\text{O}$, is formed on adding sodium acetate in excess to the syrupy liquid produced by the oxidation of moist phosphorus in the air. It crystallises in oblique rhombic prisms, which dissolve in 45 pts. of cold and 5 parts of boiling water. When gently warmed it loses its water of crystallisation, and afterwards gives off inflammable hydrogen phosphide, leaving metaphosphate. At ordinary temperatures, both the salt and its aqueous solution are perfectly stable.

Acid Potassium Hypophosphate, $\text{K}_2\text{H}_2(\text{PO}_3)_2 + \text{H}_2\text{O}$.—Hypophosphoric acid neutralised with potassium carbonate and evaporated to syrupy consistency, gave crystalline nodules, which were not analysed. On adding an equal quantity of acid, crystals of the above salt were obtained. It is soluble in twice its weight of water at ordinary temperatures, but is insoluble in alcohol. When heated, it decomposes and gives off hydrogen which burns, whilst insoluble potassium metaphosphate is left behind. It crystallises in the orthorhombic system. The crystals are small, transparent, and colourless, and a combination of the prism ∞P and the pyramid, $2\text{P}2$, with $\infty\text{P}\infty$, $\text{P}\infty$ and 0P subordinate. Cleavage parallel to $\infty\text{P}\infty$. Axes $a : b : c = 0.6792 : 1 : 0.8508$.

The normal potassium salt could not be obtained pure. A concentrated solution of this salt will detect 0.003 grm. soda dissolved in 1 c.c. of water, and existing as chloride or sulphate.

In a solution of *lithium carbonate*, hypophosphoric acid produces a crystalline precipitate very sparingly soluble in water, easily soluble in excess of hypophosphoric acid.

Normal Ammonium Hypophosphate, $(\text{NH}_4)_2(\text{PO}_3)_2 + \text{H}_2\text{O}$, is obtained by heating a 5 per cent. solution of the acid with excess of ammonia. The crystals begin to effloresce immediately after drying. They appear to consist of quadratric prisms, with pyramidal end-faces, like those of zircon; they dissolve in thirty times their weight of water, forming a strongly alkaline solution, which on evaporation gives off ammonia, soon acquires an acid reaction, and ultimately leaves acid ammonium hypophosphate. The normal salt loses ammonia even on standing in the air, the clear crystals assuming

a turbid or milky appearance. When heated, they melt, with strong evolution of ammonia, and at last with combustion of the liberated hydrogen. This latter property is peculiar to the acid hypophosphates.

Acid Ammonium Hypophosphate, $(\text{NH}_4)^2\text{H}^2(\text{PO}^3)^2$.—If the solution of the previous salt be boiled until ammonia ceases to escape, the acid ammonium salt is formed, and may be obtained in needles; it is isomorphous with the acid potassium salt.

Normal Barium Hypophosphate, $\text{Ba}^2(\text{PO}^3)^2$, is thrown down from a solution of the normal sodium salt by barium chloride as an apparently amorphous precipitate. It is very sparingly soluble in water and in acetic acid, more soluble in hydrochloric and hypophosphoric acids. It is anhydrous, and when heated changes into reddish barium pyrophosphate without any appearance of combustion. Even by very rapid heating of the damp neutral barium salt, it is not possible to effect the oxidation of the hypophosphoric acid by means of the oxygen of the water.

Acid Barium Hypophosphate, $\text{BaH}^2(\text{PO}^3)^2 + 2\text{H}_2\text{O}$, is prepared from the acid sodium salt by precipitation with barium chloride. On mixing hot solutions of 4 pts. of the acid sodium salt in 180 pts. of water, and of 5 pts. of barium chloride in 10 pts. of water, and immediately filtering, beautiful crystals were obtained on cooling. They belong to the monoclinic system, and are needles formed of 0P and ∞P , with ∞P at the end. $a:b=1.8480:1$. Angle $ac=57^\circ 4'$. They are transparent, but become turbid when heated under water. With 1000 pts. of cold water, they give a solution which has an acid reaction, and becomes turbid on boiling, in consequence of the separation of neutral or basic barium hypophosphate. The crystals scarcely suffer any loss in weight by heating at 100° , but at 140° they slowly lose the 2 mols. of water of crystallisation, and at higher temperatures pass, with combustion of escaping hydrogen, into barium metaphosphate, which melts to a white bead.

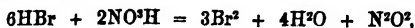
Normal Calcium Hypophosphate, $\text{Ca}^2(\text{PO}^3)^2 + 2\text{H}_2\text{O}$.—In neutral calcium solutions, neutral sodium hypophosphate, even of 200,000-fold dilution, gives rise to a perceptible turbidity. With greater concentration the solution becomes alkaline after all the calcium has been precipitated. On the contrary, on adding calcium chloride to the sodium salt, the alkaline reaction disappears with completed precipitation of the hypophosphoric acid.

After washing, the originally very gelatinous precipitate quickly becomes denser and granular, and appears under the microscope as rounded but non-crystalline particles, and by continued washing suffers another change, whereby it becomes so finely divided as to go through the thickest double or triple filters. It is insoluble in water and almost insoluble in acetic acid, but easily soluble in hydrochloric and hypophosphoric acids. The crystallisation-water is very difficult to determine, as it begins to pass off at 100° , although the salt must be brought to 200° before all can be driven off, and then slight decomposition (*i.e.* oxidation) ensues.

Acid Calcium Hypophosphate could not be obtained in the solid form, as neither dilute nor concentrated hypophosphoric acid dissolves as much neutral calcium salt as is necessary for the formation of the acid salt. As only one calcium compound of this acid appears to exist, neutral calcium solutions may be titrated with normal sodium hypophosphate after addition of red litmus tincture. Alkaline reaction sets in after completed precipitation. The same remark applies to the hypophosphates of lead and other metals.

Phosphoric Acid (Ortho-), $\text{PO}(\text{OH})^3$. **Preparation.**—In preparing this acid by the oxidation of phosphorus with nitric acid, the best results are obtained, according to Krauthausen (*Arch. Pharm.* [3], x. 410), by using nitric acid having exactly the sp. gr. 1.197. With stronger acid, the action is too violent; with weaker, the oxidation of the phosphorus is very slow.

G. F. Markoe (*ibid.* ix. 531) adds to the mixture of phosphorus and nitric acid a small quantity of bromine, or better of bromine and iodine together, whereby phosphorus pentabromide is first formed, and then decomposed by the water present into hydrobromic and phosphoric acids, $\text{PBr}_5 + 4\text{H}_2\text{O} = 5\text{HBr} + \text{PO}^3\text{H}^3$. The hydrobromic acid thus formed is immediately decomposed by the nitric acid, yielding free bromine, nitrogen dioxide, and water:



and the free bromine acts on fresh quantities of phosphorus in the same manner as before. As a convenient proportion of the several materials, Markoe recommends 1 pt. phosphorus, 6 pts. nitric acid of sp. gr. 1.42, 1 pt. water, and enough bromine to give 1 pt. of that substance to 50 pts. of phosphorus. The phosphorus is first added to the mixture of nitric acid and water, and the bromine is then added by drops, the liquid being well cooled to prevent too violent action and consequent explosion. The

danger of explosion may, however, be more effectually guarded against by using a quantity of water three times as great as that above recommended, and bringing the phosphorus and bromine together before adding the nitric acid.

Crystallised phosphoric acid melts at 41.75° (at 38.6° according to Thomsen, p. 1590), and remains liquid till cooled down to 38° , at which point it solidifies, the temperature rising simultaneously to 40.5° (Berthelot, *Bull. Soc. Chim.* [2], xxix. 3).

On the Heat of Fusion, Solution, and Formation of Orthophosphoric Acid, according to Thomsen, see p. 1590.

METALLIC PHOSPHATES. Aluminium Salts. Millot (*Bull. Soc. Chim.* [2], xxii. 242) has prepared the salts $P^2O^3 \cdot Al^2O^3 \cdot 5H^2O$, $3P^2O^3 \cdot 2Al^2O^3 \cdot 20H^2O$, and $2P^2O^3 \cdot Al^2O^3 \cdot 8H^2O$ in the same manner as the corresponding ferric salts (p. 1599).

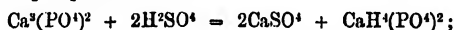
Barium Phosphate. According to Duvillier (*Compt. rend.* lxxx. 1251), this salt [also the arsenate] is decomposed by nitric acid, yielding free phosphoric [or arsenic] acid and barium nitrate. If the nitric acid be so strong that the resulting nitrate will not dissolve in it, the decomposition will be complete.

Calcium Phosphates. Tricalcic Phosphate, $Ca^3(PO^4)^2$.—A solution of this salt in aqueous carbonic acid, which is used for therapeutic purposes, may be readily prepared by passing washed carbon dioxide into water in which the recently precipitated phosphate is suspended. The filtered solution becomes turbid on exposure to the air, and more quickly when heated, from loss of carbonic acid. The clear solution has an alkaline reaction, and gives all the reactions of orthophosphates (M. Chevrier, *Compt. rend.* lxxviii. 1134).

Experiments on the action of water on tricalcic phosphate, in continuation of those already noticed (vii. 974), have been made by R. Warington (*Chem. Soc. J.* 1873, 983). By prolonged boiling, the tricalcic phosphate is converted into the salt $2Ca^2(OH)(PO^4)^2 = 3Ca^2(PO^4)^2 + Ca(OH)^2$. The solubility of tricalcic phosphate varies between 35,000 and 110,000 pts. water for 1 pt. of the phosphate. The decomposition of the salt by water begins at ordinary temperatures.

On the action of Water and other Solvents on Calcium Phosphate, gelatinous and ignited, and on Bone-substance, see BONE (p. 338).

The action of sulphuric acid on tricalcic phosphate has been examined by H. P. Armsby (*J. pr. Chem.* [2], xiii. 333), whose experiments show that when these compounds are mixed in molecular proportions, the acid acts upon only half the phosphate, forming monocalcic phosphate, thus:



and that the monocalcic phosphate then acts on the other half of the tricalcic salt, producing insoluble dicalcic phosphate, $Ca^2H^2(PO^4)^2$, thus:



See further SUPERPHOSPHATE (p. 1596).

On the composition of Bone Phosphate, see BONE (p. 337).

Dicalcic Phosphate, $Ca^2H^2P^2O^8$ or $CaHPO^4 = (OH)OP<\underset{O}{\underset{O}{\text{O}}}>Ca$, is obtained by treating the monocalcic salt with hot water or alcohol (Erlenmeyer); also by precipitating calcium chloride with ordinary disodic phosphate; the latter is the mode of preparation usually employed in pharmacy. According to Hirschsohn (*Russ. Zeitschr. Pharm.* xvi. 385), it is essential, in preparing this salt by precipitation, to add an excess of calcium chloride. In this way, not much more than half of the calcium chloride used is converted into phosphate, but if the sodium phosphate be poured not too slowly into the solution of calcium chloride kept at ordinary temperature, and the resulting calcium phosphate, immediately after precipitation, be collected on a filter, washed, and dried at a moderate heat, the whole of the sodium phosphate will be utilised, and a preparation obtained which fully satisfies the conditions of constant composition, crystalline structure, and ready solubility in dilute acids. Under the influence of strong bases it is converted into the tricalcic salt.

Hydrated Dicalcic Phosphate, $CaH^2PO^6 = CaHPO^4 \cdot 2H^2O$, or, according to Erlenmeyer, $(OH)^2P.O.Ca(OH)$, is obtained by the action of cold water on monocalcic phosphate; also by triturating 1 mol. air-dried tricalcic phosphate with 1 mol. crystallised monocalcic phosphate, the conversion being completed in about a month. When heated at 100° , it loses water very gradually, 150 hours' heating being required to bring it to a constant weight. If moistened with water four or five times a day, it attains a constant weight in about 60 hours. Heated at 100° in a stream of dry air for 36 hours, it gives off 2 mols. water; when boiled with water, it loses the same quantity in half an hour. After 24 hours' boiling in a reflux apparatus, the water

exhibited only a faint acid reaction. After an hour's boiling in a reflux apparatus with absolute alcohol, the salt remained unaltered. When heated in a sealed tube placed in a water-bath, it lost after a certain time $1\frac{1}{2}$ mol. water, and it was only after 7 hours' heating that the quantity of water given up amounted to 2 mols. (Erlenmeyer).

Monocalcic Phosphate.—According to Erlenmeyer (*loc. cit.*), this salt, when prepared by the action of cold aqueous phosphoric acid on the tricalcic salt, has the composition $\text{CaH}^2\text{P}^2\text{O}^6 = \text{CaH}^2\text{P}^2\text{O}^4 \cdot \text{H}^2\text{O}$, or $(\text{OH})^2\text{P}^2\text{O}^4 \cdot \text{Ca}^2\text{O} \cdot \text{PO}(\text{OH})^2$, and separates from the resulting solution on spontaneous evaporation in thin rhomboidal plates, leaving when ignited a somewhat porous white opaque mass, which, when heated in the blowpipe-flame, melts at the edges only to enamel-like globules. The crystallised salt contains 1 mol. water, which it gives off at 100° , but recovers on exposure to the air. According to Erlenmeyer, it is not hygroscopic, although, as observed by Birnbaum (*Jahresb. f. Chem.* 1871, 281), it takes up water and deliquesces when placed near water under a bell-jar: for on subsequent exposure to the air it gives up this water again, and acquires a constant weight. According to Birnbaum, on the other hand (*Ber.* vi. 898), it gives up only part of its water when thus exposed, and the proportion retained depends essentially on the state of humidity of the air, a maximum of atmospheric moisture corresponding to a minimum amount of phosphoric acid in the air-dried salt. The maximum difference between the amounts of phosphoric acid in the dry salt and that which had been altered by absorption of water from the air amounted to 8.8 per cent. The same variation in weight was observed under similar circumstances in a 'Noxana Superphosphate' from the manufactory of Packard and Co. in Ipswich. When drenched with somewhat less than 100 times its weight of water, it is resolved into the dicalcic salt and free phosphoric acid, $\text{CaH}^2\text{P}^2\text{O}^6 = \text{PO}^3\text{H}^2 + \text{CaHPO}^4 + \text{H}^2\text{O}$; but when a small quantity of it is introduced quickly and with agitation into 100 pts. of water, it dissolves completely in a short time. The precipitate formed on treating it with only 10 pts. water, redissolves completely in about three weeks if shaken up with the liquid every day; and that which is formed with 40 pts. water redissolves on similar treatment in a few days. But all these liquids, even that which is obtained with 1 pt. salt to 100 water, deposit a precipitate on boiling. When monocalcic phosphate was treated with cold absolute alcohol, nothing but phosphoric acid was found in solution after two days, and the residue contained lime and phosphoric anhydride in the proportion of $6\text{CaO} : 5.7\text{P}^2\text{O}^5$. By boiling the salt for an hour in a reflux apparatus with 50 times its weight of absolute alcohol, it is completely resolved into free phosphoric acid which dissolves in the alcohol, and insoluble CaHPO^4 . The same result was obtained with 30 pts. of absolute alcohol after two hours' boiling. Absolute ether dissolves the pure salt without alteration, and a specimen contaminated with adhering mother-liquor may be completely purified by agitation with ether.

Decomposition by Sodium Carbonate.—According to Frebault a. Destrem (*Bull. Soc. Chim.* [2], xxvii. 499), the reaction between monocalcic phosphate and sodium carbonate consists not, as generally supposed, in the separation of calcium carbonate and formation of sodium phosphate, but in the division of the phosphoric acid between the lime and the soda, and the elimination of the whole of the carbon dioxide as gas, so that it is correctly represented by the following equation proposed by Thénard, Soubeiran, and Lécaneu:



That the calcium phosphate cannot be decomposed by the sodium carbonate in such a manner as to form sodium phosphate and calcium carbonate, is plainly shown by the fact that calcium carbonate is, on the contrary, decomposed by sodium phosphate, with formation of basic calcium phosphate, together with sodium carbonate and free carbon dioxide at high and of sodium bicarbonate at low temperatures. The carbonates of barium, manganese, zinc, and magnesium are decomposed in like manner by sodium phosphate.

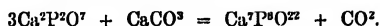
Superphosphate. The agricultural value of this mixture of monocalcic phosphate and gypsum, prepared by treating ground bones with sulphuric acid (iv. 555), depends on the proportion of soluble phosphate which it contains. Now this amount is found to decrease in course of time, in consequence of the gradual reconversion of the soluble into insoluble phosphate, and the change—known as 'retrogression'—is sometimes attributed to the formation of dicalcic phosphate by the action of the monocalcic salt on undecomposed tricalcic phosphate contained in the mixture. A. Millot, however (*Compt. rend.* lxxviii. 1134; lxxxi. 522; *Ber.* viii. 187), infers, from experiments in which 1 mol. pure tricalcic phosphate was treated with 2 and with 1 mol. sulphuric acid, that the reaction just mentioned takes place only when the quantity of sulphuric acid used is insufficient for the decomposition of the bone-ash,

and consequently the product does not contain any free phosphoric acid. In presence of free phosphoric acid, dry monocalcic phosphate is not resolved by heat into the dialcic salt and free phosphoric acid. The retrogradation in solubility of the phosphoric acid in superphosphate is especially attributed by Millot to the presence of ferric oxide, alumina, and magnesia. A superphosphate prepared from the coprolites of the Ardennes, in which all the phosphoric acid was originally in the soluble state, was found after two years to contain only 10 per cent. soluble phosphoric acid, the remaining 90 per cent. having become insoluble. On washing this phosphate with hot water till all the gypsum was removed, the residue was found to be free from lime and to consist of the phosphates $\text{Fe}^2\text{O}^3 \cdot 2\text{P}^2\text{O}^5$ and $2\text{Fe}^2\text{O}^3 \cdot 3\text{P}^2\text{O}^5$.

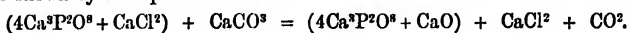
A. Rümpler observes (*Zeitschr. anal. Chem.* vi. 151) that in superphosphates obtained by decomposition of phosphorites containing iron or alumina, a soluble ferric or aluminic phosphate is often formed, having the composition $\text{Fe}^2\text{O}^3[\text{PO}(\text{OH})^2]^6$ or $\text{Al}^2\text{O}^3[\text{PO}(\text{OH})^2]^6$, and that when this phosphate is treated with a large quantity of water, it is decomposed, with separation of neutral phosphate, $\text{M}^2\text{O}^3(\text{PO}^4)^2$, so that the results obtained in estimating the 'soluble' phosphoric acid are too low, and the more so as the quantity of water used in the digestion is greater. From numerous experiments bearing on this matter, Rümpler infers that in analysing superphosphates, the best mode of extracting from them the largest quantity of phosphoric acid is to lixiviate them with the minimum quantity of water, and not, as is the usual practice, to make up a given quantity of superphosphate with water to a litre and take an aliquot part of the liquid for the estimation of the phosphoric acid.

On the Analysis of Superphosphates, see also Joulie (*Compt. rend.* lxxvi. 631; *Chem. Soc. J.* 1873, 766); Erlenmeyer (*Ber.* ix. 1839; *Jahresb. f. Chem.* 1876, 984; *Chem. Soc. J.* xxxi. 759); Albert a. Siegfried (*Zeitschr. anal. Chem.* 1877, 182; *Jahresb. f. Chem.* 1877, 1044).

Action of Heat on Mixtures of Calcium Phosphates and Calcium Carbonate.—Pyro- and orthophosphates of calcium, as well as phosphates of the apatite class, are decomposed by ignition with calcium carbonate, in such a manner that part of the calcium oxide in the latter enters into chemical combination with the phosphate, and is not reconverted into CaCO^3 by the action of ammonium carbonate. The extent of this decomposition varies according to the proportions of the mixture, the intensity and duration of the ignition, and is considerably increased by a high temperature and the presence of organic matter. This mode of decomposition is determined, in the case of calcium pyrophosphate, by the tendency of that salt to pass into normal orthophosphate; in the case of the normal orthophosphates, by their tendency to form basic salts; and in apatites and similar compounds by the interchange between CaCl^2 and CaO . A strongly ignited mixture of 6 pts. pyrophosphate and 1 pt. carbonate yielded, after the CaO had been completely washed out with water, a residue of phosphate which was somewhat difficult to dissolve in nitric acid, and had the composition $7\text{CaO} \cdot 3\text{P}^2\text{O}^5 = \text{Ca}^7\text{P}^6\text{O}^{22}$; its formation may accordingly be represented by the equation:



Experiments with normal orthophosphate led to the formation of a salt having the composition $\text{Ca}^3\text{P}^2\text{O}^8 + \frac{1}{2}\text{CaO}$ or $5\text{Ca}^3\text{P}^2\text{O}^8 + \text{CaO}$. Apatite was decomposed in the manner shown by the equation:



These results indicate the necessity of determining the CO^2 in mineral phosphates before ignition; and as bones comport themselves like a mixture of calcium orthophosphate and carbonate with organic matter, there is no reason to suppose that they contain a substance having the composition $\text{CaO} \cdot 3\text{Ca}^3\text{P}^2\text{O}^8$, as assumed by Aebv (F. Wibel, *Ber.* vii. 220). See Bone (p. 337).

Native Calcium Phosphates.—The following analyses of mineral phosphates and superphosphates used in England for agricultural purposes have been published by W. C. Reid (*Chem. News*, xxxiv. 48, 55).

1-5. Cambridge coprolites from the upper greensand of Cambridgeshire: grey hard nodules, consisting either of true coprolites or of concretions formed round bones. 6, 7, 8. Coprolites from Boulogne. 9-12. Pseudocoprolites from Suffolk: calcareous concretions impregnated with phosphates. 13. Coprolites from Bedfordshire. 14. Lenticular coprolites, a poor variety from Cambridgeshire. 15 and 16. Russian coprolites. 17. South Carolina and Charleston phosphates of high value. They are obtained from chalk-beds, and form irregular nodules enclosing animal remains and imbedded in clay. 18 and 19. Lot or Bordeaux phosphates from the Departments Lot and Lot-et-Garonne, where they occur in veins and thin layers of a limestone. The analyses relate to the best and a poorer quality. 20 and 21. Nassau phosphorites,

ordinarily very rich in iron; not much in request of late. The analyses give the extremes between which the actual values generally fluctuate. 22-25. Spanish and Portuguese phosphorites, usually classed together as Estremadura phosphorite. 26, 27. Norwegian, and 28, Canadian apatite, forming veins in crystalline rocks; exported to England in small quantities only. 29 and 30. Sombrero guano, really a phosphorite; formerly imported in considerable quantity, lately but seldom. The two analyses give extreme values. 31 and 32. Navassa guano, a similar material from the island of Navassa. In this case also the analyses give extreme values.

Composition of Native Calcium Phosphates.

	Ca ³ P ² O ⁸	CaCO ³	Fe ² O ³ , Al ² O ³		CaF ²	CaCl ²	Insoluble Silicates
1.	60.87	18.25	5.30	1.80	—	—	6.50
2.	58.52	12.47	3.49	2.20	—	—	6.04
3.	27.12*	11.66	4.44	3.00	—	—	6.22
4.	54.89	15.13	3.82	4.00	—	—	8.64
5.	57.09	13.27	3.24	4.33	—	—	6.93
6.	46.45	11.93	7.29	2.08	—	—	23.56
7.	48.0	20.00		—	—	—	28.1
8.	43.3	22.90		—	—	—	28.2
9.	53.4	17.5	10.4	1.4	—	—	9.7
10.	61.3	11.6	4.8	3	—	—	10
11.	52.5	12.2	8.5	4.3	—	—	12.2
12.	56	10	8	3	—	—	12
13.	50	8	8	4	—	—	20
14.	36	10	12	3	—	—	28
15.	33	5.5	6	3.5	—	—	43
16.	48	12		—	—	—	30.5
17.	54	14	3.5	2.5	—	—	15
18.	67.19	15.31	4.20	—	—	—	5.2
19.	55.45	8.30	12.86	—	—	—	19.13
20.	58	5	10	—	—	—	10
21.	65	8	15	—	—	—	12
22.	72	9	3.5	3.5	—	—	4
23.	78.7	—	8.8	—	—	—	11.4
24.	72.6	—	5.1	—	—	—	18.3
25.	80.6	4.2	2.0	—	—	—	12.3
26.	90.74	—	2	—	1.61	—	1.64
27.	91.13	—	—	1.59	4.28	—	—
28.	91.20	—	—	7.60	0.78	—	0.9
29.	69	2	7	1.5	—	—	1
30.	76	4	10	1.8	—	—	2
31.	55	4	23	1	—	—	4
32.	70	6	28	2	—	—	5

* Probably a misprint for 57.12.

A phosphorite from Rossberg near Rossdorf in Hesse-Darmstadt was found by P. Wagner (*Ber. d. landw. Versuchsst. Darmstadt*, 1874) to contain 38.92 per cent. phosphoric acid; another from Oberamstadt, Hesse-Darmstadt, yielded 23.2 per cent. phosphoric acid, 19.6 silica, and 8.6 alumina. A guano from Australia yielded 60.70 per cent. calcium phosphate containing 2.78 phosphoric acid.

Several samples of phosphorite from Logrosan, Estremadura, very large quantities of which are imported into Germany by way of Hamburg (more than 11000 kg. in 1872), have been analysed by B. Niederstadt (*Ber.* vii. 107). It has the advantage over many others of containing only small quantities of ferric oxide and alumina, so that the retrogression of soluble into insoluble phosphates does not take place in it to any great extent. It contains, however, a large amount of silica:

$\text{Ca}^*\text{P}^*\text{O}^*$	$\text{Mg}^*\text{P}^*\text{O}^*$	CaCO_3^*	CaSO_4^*	Fe^*O^*	Al^*O^*	CaF^*	SiO^*	H^*O
54.691	7.010	8.065	1.200	0.621	0.165	1.520	25.720	0.250 = 99.242
62.352	1.605	13.688	2.440	0.528	0.985	1.204	16.412	0.175 = 99.389
57.369	0.708	7.385	1.599	0.453	0.405	1.822	29.428	0.790 = 99.959
59.594	3.977	13.327	0.858	0.910	0.427	0.983	19.164	0.721 = 99.961

Calcium phosphate from Ciply, in Belgium, containing 20.35 per cent. P^*O^* , has been analysed by Nevoit (*Compt. rend.* lxxix. 256; *Chem. Soc. J.* 1874, 1146).

On Apatite, see p. 116.

Calcio-uranic Phosphate, $(\text{CaO} \cdot 2\text{UO}_3)\text{P}^*\text{O}^* + 8\text{H}^*\text{O}$. *Uranite Autunite* (iv. 585). This mineral has lately been examined by Church (*Chem. Soc. J.* 1875, 109) with special reference to its amount of water.

Analyses.—1 and 2. Sulphur-yellow crystals from Cornwall. 3 and 4. Crusts about half an inch thick, composed of irregularly grouped yellow crystals from Autun. 5. Smaller crystals from Autun, having a deeper sulphur-yellow colour :

	1	2	3	4	5
Water lost over Sulphuric acid . . .	not det.	8.24	9.08	8.38	9.48
„ in a vacuum . . .	„	not det.	5.28	not det.	4.95
„ at 100° . . .	13.8	6.90	not det.	7.29	0.75
„ at a red heat . . .	4.85	4.12	5.28	4.02	5.15
Uranic oxide . . .	60.00	not det.	61.34	not det.	60.87
Lime . . .	5.01	—	5.24	—	5.31
Phosphoric anhydride . . .	13.84	—	14.97	13.66	13.40

From the constancy of the loss of water in dry air and in the vacuum, it may be inferred that this water is not merely hygroscopic, but chemically, though loosely combined; and this view is corroborated by the fact that the crystals, in parting with this water, undergo physical alteration, becoming opaque and brittle. The numbers show that uranite in its original state contains 10 mols. H^*O , of which 6 mols. are given off under the air-pump.

Cerium Phosphates. Monazite from Arendal, in large dull crystals, free from thorium, has been analysed by Rammelsberg (*Jahrb. f. Min.* 1877, 831). A. Direct result of analysis. B. Corrected for admixtures. C. Values calculated according to the formula $(\text{Ce}, \text{La}, \text{Di})^2\text{P}^*\text{O}^*$, in which $\text{Ce} : (\text{La}, \text{Di}) = 2 : 3$; and $\text{Ce} = 138$; $\text{La}, \text{Di} = 140$.

P^*O^*	Ce^*O^*	$\text{La}^*\text{O}^*, \text{Di}^*\text{O}^*$	Fe^*O^*	CaO	SiO^*
A. 28.78	27.73	39.24	1.30	0.90	1.60 = 99.55
B. 29.92	28.82	40.79	—	—	— = 99.53
C. 30.28	27.72	42.00	—	—	— = 100

Sp. gr. = 5.174.

According to these results, monazite free from thorium must be identical with cryptolite (iv. 558).

P. v. Jeremejew (*Zeitschr. Kryst.* i. 398) describes crystals of monazite from the Ilmen mountains, exhibiting combinations of the forms $\infty\text{P}\infty$, $\infty\text{P}\infty$, ∞P , $+\text{P}\infty$, $\text{P}\infty \cdot 0\text{P}$, and twins according to 0P .

An analysis of turnerite by F. Pisani (*Jahrb. f. Min.* 1877, 412), made on a very small quantity of material, gave the approximate values P^*O^* 28.4, CeO 59.1, LaO 8.9 = 96.4, showing the identity of turnerite with monazite.*

Chromic Phosphate. The violet modification of this salt, $\text{Cr}^2(\text{PO}_4)^3 + 12\text{H}^*\text{O}$, gives off $7\text{H}^*\text{O}$ at 100°, and is converted into the green modification; with nitric and sulphuric acids it behaves like the violet sulphate (Etard, p. 458).

Glucinum Phosphate, $\text{Gl}^1(\text{PO}_4)^2$, is precipitated on adding ordinary disodic phosphate to a solution of normal glucinum sulphate (Atterberg, *Bull. Soc. Chim.* [2], xix. 497).

Iron Phosphates. When sodium phosphate and ferrous sulphate are enclosed, together with carbon dioxide and a little water, in a sealed tube, the ferrous phosphate produced by double decomposition of the two salts is coloured blue (even in the dark) by the action of carbon monoxide formed by reduction of the dioxide. About one-sixth of the carbon dioxide is thus reduced in a few days. An ethereal solution of chlorophyll is separated by hydrochloric acid into two layers, the upper of which

* Turnerite was originally regarded as a silicate (v. 918).

contains iron, lime, and phosphoric acid—that is to say, the constituents of vivianite (E. N. Horsford, *Ber.* vi. 1390).

Ferric Phosphates (Millot, *Bull. Soc. Chim.* [2], xxii. 242).—The well-known precipitate obtained on adding ordinary sodium phosphate in excess to a *ferric salt* has the composition $\text{Fe}^2\text{O}^3 \cdot \text{P}_2\text{O}^5 + 5\text{H}^2\text{O}$ or $\text{Fe}^2(\text{PO}^4)^2 + 5\text{H}^2\text{O}$, and yields on ignition the anhydrous salt $\text{Fe}^2(\text{PO}^4)^2$, which is insoluble in water and is decomposed by alkalis.

The salt $2\text{Fe}^2\text{O}^3 \cdot 3\text{P}_2\text{O}^5 + 10\text{H}^2\text{O}$, first prepared by Rammelsberg, is obtained easily and in any required quantity by treating ferric oxide with excess of phosphoric acid, either at ordinary or at higher temperatures, adding water, filtering, heating the filtrate to the boiling point, and drying the resulting precipitate at 100° . This salt gives off all its water at a red heat, and is then no longer soluble in acids. The salt $\text{Fe}^2\text{O}^3 \cdot 2\text{P}_2\text{O}^5 + 8\text{H}^2\text{O}$ is obtained by heating the last with 2 mols. phosphoric acid.

According to G. W. Waine (*Chem. News*, xxxvi. 132), the ferric phosphate obtained by precipitating ferric chloride with sodium phosphate always has the composition $2\text{FePO}^4 + 5\text{H}^2\text{O}$ or $\text{Fe}^2\text{O}^3 \cdot \text{P}_2\text{O}^5 + 5\text{H}^2\text{O}$, whether it be obtained by adding ferric chloride to excess of sodium phosphate, or sodium phosphate to excess of ferric chloride.

On *Andrewsite*, a native iron phosphate from Cornwall, see p. 84.

Lead Phosphates are decomposed by nitric acid, with formation of lead nitrate and free phosphoric acid, the decomposition being complete if the nitric acid is of such a strength that the lead nitrate will not dissolve in it (Duvillier, *Compt. rend.* lxxxi. 1251). Lead phosphate is easily decomposed by excess of *potassium iodide*, with formation of lead iodide or the double iodide of lead and potassium (Campani, *Gazz. chim. ital.* 1876, 461).

Magnesium Phosphate. A compound of magnesium-hydrogen orthophosphate with nitrogen tetroxide, $4\text{MgHPO}^4 \cdot \text{N}_2\text{O}^4$ is obtained by dissolving magnesium pyrophosphate in nitric acid of sp. gr. 1.25; keeping the solution nearly at the boiling heat for some time to convert the pyrophosphate into orthophosphate; then evaporating to dryness on a sand-bath; reducing the white, gummy, fissured acid residue to coarse powder; and heating it somewhat more strongly—best in a paraffin-bath—till it assumes a rusty-brown colour, and ceases to give off acid fumes. The compound thus prepared is a crystalline powder, whitish-yellow at ordinary, rusty-brown at higher temperatures, and becoming whitish-yellow again on cooling. When strongly heated it gives off water and nitrogen tetroxide, and leaves a residue of magnesium pyrophosphate (E. Luck, *Zeitschr. anal. Chem.* vii. 255).

Manganese Phosphates. These salts have been examined by Erlenmeyer and Heinrich (*Liebig's Annalen*, exc. 189).

Monomanganous Phosphate, $\text{MnH}^2(\text{PO}^4)^2 + 2\text{H}^2\text{O}$, previously obtained by Heintz (iv. 571), is prepared by dissolving recently precipitated manganous sulphide in excess of phosphoric acid, leaving the solution to crystallise, and removing the mother-liquor by washing with ether free from water and alcohol. At 100° it gives off water, and is partially decomposed, with separation of phosphoric acid. It remains unaltered in dry air, but deliquesces in moist air, forming an acid liquid from which crystals of the dimanganous salt separate out. The same change takes place when the monomanganous salt is treated with cold water, so that Heintz's statement that this salt is easily soluble in water cannot be regarded as correct.

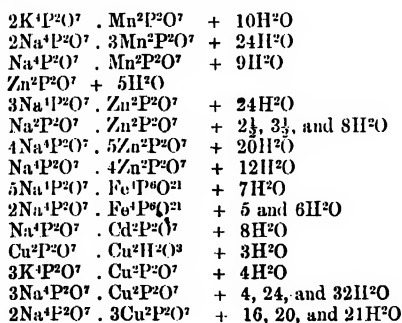
Dimanganous Phosphate, $\text{Mn}^2\text{H}^2(\text{PO}^4)^2 + 6\text{H}^2\text{O}$, or $\text{MnHPO}^4 + 3\text{H}^2\text{O}$, may be obtained by methods already described (iv. 571), or, according to Debray (*Ann. Chim. Phys.* [3], lxi. 433), by treating manganese carbonate with aqueous phosphoric acid, and heating the resulting solution to 70° —or in larger quantity and better crystals by heating the same solution with alcohol till it becomes turbid, and then leaving it to itself for awhile. The crystals thus obtained are, according to Haushofer's measurements, orthorhombic, having the axial ratio, $a : b : c = 0.9445 : 1 : 0.9260$, and mostly exhibiting the combination $\infty\text{P}\infty \cdot \infty\bar{\text{P}}\infty \cdot 0\text{P} \cdot \text{P} \cdot \frac{1}{2}\text{P} \cdot \frac{1}{2}\bar{\text{P}}\infty$. An anhydrous dimanganous phosphate, $\text{Mn}^2(\text{PO}^4\text{H})^2$, is obtained by boiling the monomanganous salt with alcohol.

Trimanganous Phosphate, $(\text{Mn})^3(\text{PO}^4)^2 + 7\text{H}^2\text{O}$, is obtained in indistinct crystals by precipitating manganous sulphate with excess of disodic phosphate: it gives off half its water over sulphuric acid. A trimanganous phosphate, differing somewhat from the preceding in the manner in which it gives off its water of crystallisation, is obtained in needle-shaped crystals by treating the dimanganous salt with cold water. It effloresces on exposure to the air, the effloresced product containing from 9 to 11 mols. water according to the degree of moisture of the air. Over sulphuric acid, however, it is likewise converted into the salt with 7 mols. H^2O .

A *pentamanganous phosphate*, $\text{Mn}^5\text{H}^2(\text{PO}^4)^4 + 4\text{H}^2\text{O}$, is obtained by filtering the liquid resulting from the decomposition of the monomanganous salt by water, and keeping it for some time at the boiling heat. It then separates in rose-coloured, rather large and well-defined crystals, which give off their water at 150° , and become opaque, without melting, at a red heat. According to Haushofer's measurements, they are monoclinic. Axial ratio $a : b : c = 1.9927 : 1 : 1.7122$. Angle $ac = 82^\circ 26'$. Combination $\infty \text{P} . \text{OP} . \frac{1}{2}\infty$. The prismatic faces are vertically striated. Many crystals likewise exhibit the positive hemidome $\frac{1}{2}\infty$ (Erlenmeyer).

When pure manganese dioxide or a permanganate is dissolved at 100° – 110° in syrupy phosphoric acid, a dark amethyst-blue syrup is obtained which is dissolved in all proportions by water, with ruby-red colour (Barreswil's test, *Compt. rend.* xlii. 677); and on heating the solution in the water-bath, it becomes colourless, and deposits a greyish-green muddy precipitate of a peculiar phosphate, which when dried at 106° forms a light greenish-grey powder, appearing under the microscope crystalline and slightly double-refractive. It is insoluble in water, but when boiled with hydrochloric acid, it forms, with evolution of chlorine, a clear light yellow solution containing nothing but manganese and phosphoric acid. From this and the following phosphates, ammonium sulphide throws down the manganese, not as a flesh-coloured hydrated sulphide, but as a blackish-green anhydrous sulphide. At a low red heat, this phosphate gives off a considerable quantity of water, and assumes a brownish ash-grey colour. At 100° – 110° it redissolves in syrupy phosphoric acid, producing the original amethyst-red liquid. On saturating phosphoric acid with this phosphate at the same temperature, and concentrating the solution on the sand-bath, a *second* phosphate is deposited in six-sided plates or tabular rhombohedrons, or rhombic dodecahedrons, $\frac{1}{2}$ mm. in size, strongly lustrous, double-refracting, amethyst-coloured when hot, dark ruby-red at ordinary temperatures. These crystals, which are insoluble in water, are perhaps identical with peach-blossom coloured manganic metaphosphate. By concentrating the amethyst-blue phosphate over a gas-flame at a low red heat, a *third* phosphate is obtained in the form of a honey-yellow transparent glass, soluble in all proportions in water; and on finally driving off the excess of phosphoric acid at a red heat, a *fourth* phosphate is left, in the form of brilliant grey needle-shaped crystals, infusible, and permanent in the fire (W. H. Laspeyres, *J. pr. Chem.* [2], xv. 320).

PYROPHOSPHATES, $\text{M}^2\text{P}^2\text{O}^7 = (\text{M}')^2\text{OP} . \text{PO}(\text{OM}')^2$. A number of these salts, principally double salts, have been prepared by C. N. Pahl (*Ber.* vi. 1465), in most cases by dissolving the pyrophosphate of a heavy metal in a solution of an alkaline pyrophosphate. The following have been analysed :



The following table exhibits the specific gravities of several pyrophosphates, as determined by pupils of F. W. Clarke (*Sill. Am. J.* [3], xiv. 281):

Salt	Specific gravity	Determined by
$\text{Na}^1\text{P}^2\text{O}^7$	$\left. \begin{array}{l} 2.3851^* \\ \text{and } 2.3613 \end{array} \right\}$ at 17°	C. A. Mohr
$\text{Na}^1\text{P}^2\text{O}^7 + 10\text{H}^2\text{O}$	1.7726^\dagger " 21°	"
$\text{Mg}^2\text{P}^2\text{O}^7$	$\left\{ \begin{array}{l} 2.5981 \\ 2.559 \end{array} \right.$ " $\left. \begin{array}{l} 22^\circ \\ 23^\circ \end{array} \right\}$	G. W. Lewis
$\text{Mn}^2\text{P}^2\text{O}^7$	$\left\{ \begin{array}{l} 3.5847 \\ 3.5742 \end{array} \right.$ " $\left. \begin{array}{l} 20^\circ \\ 26^\circ \end{array} \right\}$	"

* Schröder found 2.534.
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† Playfair & Joule found 1.83.
5 L

‡ Schröder found 2.22.

Salt	Specific gravity	Determined by
$Zn^2P^2O^7$	$\left\{ \begin{array}{l} 3.7538 \\ \text{and } 3.7573 \end{array} \right\}$ at 23°	G. W. Lewis
$Co^2P^2O^7$	$\left\{ \begin{array}{l} 3.746 \\ 3.710 \end{array} \right\}$ " 23° " 25°	"
$Ni^2P^2O^7$	$\left\{ \begin{array}{l} 3.9308 \\ 3.9064 \end{array} \right\}$ " 25° " 27°	"

For sodium metaphosphate, $NaPO_3$, C. A. Mohr 2.4756 at 19.5° and 2.4769 at 18° ; for potassium metaphosphate, KPO_3 , 2.2639 and 2.2513 at 14.5° ; for trisodic orthophosphate, Na_3PO_4 , 2.5111 at 12° and 2.5362 at 17.5° .

Double pyrophosphates of lithium with sodium and potassium have been prepared by Kraut, Nahnsen a. Cuno (*Liebig's Annalen*, cxxxii. 165). Mixtures of the aqueous solutions of sodium pyrophosphate and lithium chloride, when left at rest at ordinary temperatures, deposit a double salt only when the lithium pyrophosphate is in excess; when the mixtures are heated, a precipitate of the double salt is also formed more quickly in proportion as the quantity of lithium salt is greater. With an excess of sodium salt, the formation of a crystalline precipitate takes place only after prolonged boiling. The composition of the precipitates differs according to the proportion of the two salts present in the solution. Double pyrophosphates of lithium and potassium are formed in the same way, but less readily.

When calcium pyrophosphate is exposed for several hours to a dull red heat, and the fused mass is stirred with an iron spatula, a perfectly transparent glass is obtained which after cooling exactly resembles ordinary glass in appearance, has a density of 2.6, and a refractive power equal to that of crown-glass (1.525). It may be worked like ordinary glass into prisms, lenses, &c., and cut and ground into various forms. It does not dissolve any metallic oxides except those of cobalt and chromium. It resists the action of acids at ordinary temperatures, but is attacked by them when heated; also by potash. On the other hand, it completely withstands the action of hydrofluoric acid, and may therefore be used for making spectacles for workmen who are exposed to the fumes of that acid; it may also be applied to the making of enamel (Sidot, *Compt. rend.* lxxxiv. 1501).

PHOSPHORIC ETHERS. On the action of Ethyl Phosphate on the Chlorides of Phosphorus, see p. 1589.

Phenylphosphoric Acids and Chlorides (Jacobsen, *Ber.* viii. 1519).

Monophenylphosphoric Chloride, $PO(OC^6H^5)Cl^2$, is formed by adding 1 mol. phenol to 1 mol. $POCl^3$, then heating, distilling, and fractionating. It boils at 241° – 243° , and is converted by access of moisture into

Monophenylphosphoric Acid, $PO(OC^6H^5)(OH)^2$.—This acid forms thick deliquescent needles melting at 97° – 98° . During the concentration of its solution it partly decomposes into phenol and phosphoric acid. By distillation it is resolved into phenol and metaphosphoric acid. Its barium salt is very soluble in water, and crystallises in transparent prisms.

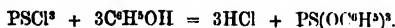
Diphenylphosphoric Chloride, $PO(OC^6H^5)^2Cl$, produced by the action of several molecules of phenol on 1 mol. $POCl^3$, boils at 314° – 316° (bar. at 272 mm.), and offers a somewhat considerable resistance to the action of alkalis.

Diphenylphosphoric Acid, $PO(OC^6H^5)^2OH$, formed from it, is an oily liquid slightly soluble in water and in alcohol. Its sodium salt crystallises in transparent needles.

Triphenyl Phosphate, $PO(OC^6H^5)^3$, formed in the last-mentioned reaction, together with diphenylphosphoric chloride, crystallises in slender needles, melts at 45° , and boils at a very high temperature. It is insoluble in water, but dissolves readily in alcohol (Jacobsen).

Benzyl-phenyl Phosphate, $(C^6H^5H^1)^2PO^4 = PO[OC^6H^4(C^6H^7)]^2$, is obtained by heating benzyl-phenol, $C^6H^4(C^6H^7)OH$, on the water-bath with phosphorus pentachloride, and decomposing the product with water. When purified by washing with a small quantity of ether, it forms white crystals, slightly soluble in ether, more readily in alcohol and in chloroform, melting at 93° – 94° (Paternò a. Fileti, *Gazz. chim. ital.* vi. 121).

Triphenyl Monothiophosphate, $PS(OC^6H^5)^3$, is prepared by boiling a mixture of phosphorus thiochloride (1 mol.) and phenol (3 mols.) in a reflux apparatus till the liquid assumes a darker colour, then treating the cooled product with soda-ley, and crystallising it from alcohol:



This ether forms small white needle-shaped crystals which turn red on exposure to light, but lose this colour when kept in the dark. It is insoluble in water, but soluble in ether, chloroform, benzene, and carbon sulphide. It melts at 40° , and boils with decomposition at a temperature above 360° . On mixing its alcoholic solution with a solution of thallous oxide, thallium sulphide is precipitated and triphenyl-phosphate is produced. The thio-ether is not altered by boiling with water. Strong nitric acid does not act upon it, but the red fuming acid oxidises it partially, with separation of a red oil, and completely when heated with it under pressure (P. Schwarze, *J. pr. Chem.* [2], x. 222).

Triphenyl Trithiophosphate, $\text{PO}(\text{SC}^{\circ}\text{H}^{\circ})^3$, is formed on boiling phosphorus oxychloride with phenyl-mercaptan, and separates after some time from the cold-saturated alcoholic solution in well-defined prisms, apparently monoclinic. It is insoluble in water, but dissolves in alcohol, ether, benzene, chloroform, and carbon sulphide, melts at 72° , and boils with decomposition at a temperature above 360° . With nitric acid it reacts like the monosulphuretted ether. It is decomposed by gentle heating with water, a mixture of acid phenyl-ethers of thiophosphoric acids passing into solution, while a mixture of neutral ethers remains undissolved (Schwarze).

Triphenyl Tetrathiophosphate, $\text{PS}(\text{SC}^{\circ}\text{H}^{\circ})^3$, prepared with phenyl mercaptan and phosphorus thiochloride, forms white needles having a silky lustre, and melting at 86° . It is insoluble in water, but dissolves in alcohol, ether, benzene, chloroform, and carbon sulphide. It does not volatilise without decomposition. With water and with nitric acid, it reacts like the monothiophosphoric ether. Attempts to convert it into triphenylphosphine by the action of metals (bismuth, copper, thallium) were unsuccessful (Schwarze).

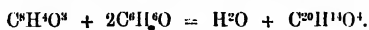
PHOSPHORUS SULPHIDES (G. Ramme, *Ber.* xii. 1350). *Phosphorus pentasulphide* is obtained in pale yellow prisms, by heating in sealed tubes at 210° for eight hours a solution of sulphur and common phosphorus in carbon bisulphide. Attempts to prepare the trisulphide P^3S^3 by this method, or by heating a mixture of amorphous phosphorus and sulphur, were unsuccessful, the product in each case consisting of the disulphide P^3S^2 , or, according to its vapour-density, P^3S^6 . *Phosphorus disulphide* crystallises in pale yellow transparent needles, which melt at 296° – 298° .

Heated with water at 150° , it yields phosphorous, phosphoric, and hydrosulphuric acids. The compound P^3S^3 is obtained by heating a mixture of sulphur and red phosphorus in a tube at 260° , or by heating P^3S^6 with common phosphorus in a current of carbonic anhydride at 320° . It dissolves freely in carbon bisulphide, and separates from the solution, on evaporation, in pale yellow prisms melting at 166° .

The substance described by Berzelius as P^3S^{12} (iv. 605) is not a definite compound, but consists of crystals of sulphur mixed with a small quantity of phosphorus. The liquid sulphides of phosphorus mentioned by Berzelius are mixtures of sulphur and phosphorus, which are separated by distillation with water.

PHTHALANILS. Syn. with PHENYL-PHTHALIMIDES (see PHTHALIMIDES).

PHTHALEÏNS and **PHTHALINS** (vii. 977). 1. **Phenol-phthaleïn**, $\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}$ (A. Baeyer, *Ber.* ix. 1230; xii. 642). This compound is obtained: (1). By the action of phthalic anhydride on phenol in presence of sulphuric acid:

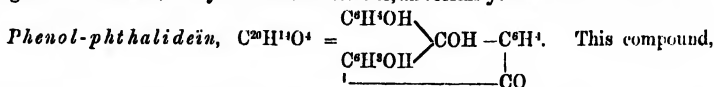


Five parts of phthalic anhydride, 10 pts. phenol, and 4 pts. strong sulphuric acid are heated at 120° for ten hours, the resulting mass is boiled with water, and the residue dissolved in dilute soda-ley. On filtering the liquid, the anhydride of phenol-phthaleïn remains undissolved, and the filtrate mixed with acetic acid and a small quantity of hydrochloric acid, deposits the phthaleïn, which may be purified by solution in alcohol and boiling with animal charcoal. The alcoholic solution mixed with water and heated to the boiling point deposits the phthaleïn in the form of a white or yellowish granulo-crystalline powder. From the aqueous mother-liquors or from a solution in over-heated water, it may be obtained in larger crystals, which, according to Groth, are triclinic.

(2). From Diphenyl-phthalide, $\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}$, formerly called *Phthalophenone* (p. 1619). When this compound is added at ordinary temperatures to fuming nitric acid, a mixture of isomeric *dinitrodiphenyl-phthalides* is obtained, which, by reduction with tin and hydrochloric acid, yields a mixture of diamido-compounds; and on removing the tin by hydrogen sulphide, precipitating with sodium carbonate, and dissolving the resulting precipitate in hot alcohol, the solution on cooling deposits a *diamidodiphenyl-phthalide*, $\text{C}^{\circ}\text{H}^{\circ}\text{O}^{\circ}(\text{NH}^{\circ})^2\text{O}^{\circ}$, in thick plates having an adamantine lustre and melting at 179° – 180° , the mother-liquor when concentrated

formed by the action of sulphuric acid on phenol-phthalin, and is thrown down by water from the acid solution in the form of an amorphous yellowish precipitate, which dissolves readily in ether to form a yellow solution with greenish fluorescence. It is not crystallisable, and oxidises easily in the air, so that it cannot well be analysed; but the composition of the bromine-derivative described below shows that its formula is $C^{20}H^{14}O^8$, and consequently that it is formed by elimination of water from phenol-phthalin, into which substance it is reconverted by heating it with water at 175° . It dissolves in alkalis without alteration in the absence of air.

Tetrabromophenol-phthalidin, $C^{20}H^{10}Br^4O^4$, is thrown down by water from a solution of the tetrabromophenol-phthalin in strong sulphuric acid, as a yellow precipitate, which crystallises from alcohol in yellow needles. It dissolves sparingly in alcohol and glacial acetic acid, freely in ether and acetone, and forms yellow solutions in alkalis.



metameric with phenol-phthaloin and related to phenol-phthalidin in the same manner as triphenyl-carbinol to triphenyl-methane, is produced by oxidation of phenol-phthalidin, the best reagent for the purpose being potassium manganate in alkaline solution. It crystallises from glacial acetic acid in colourless, thin, tabular crystals, and from weak spirit in thin laminae, which melt at 212°. It dissolves in potash-ley, with yellow colour, and is precipitated from the solution in colourless amorphous flocks by acids. It forms a deep violet solution with sulphuric acid, the smallest portion of phthalidein being enough to colour a large quantity of the acid. Its alkaline solution is reduced by zinc-dust to phenol-phthalidin.

Diacetyl-phenol-phthalideïn, $\text{C}^{20}\text{H}^{12}\text{O}^4(\text{C}^2\text{H}^3\text{O})^2$, obtained by boiling phenol-phthalideïn with acetic anhydride, crystallises in small prisms melting at 109° .

Phenol-phthalidein chloride, $C^{20}H^{12}O^2Cl^2$, formed by the action of phosphorus pentachloride on phenol-phthalidein at 125° , crystallises from alcohol in silky needles, which melt at 156° .

Tetrabromophenol-phthalideïn, $\text{C}^{20}\text{H}^{10}\text{Br}^4\text{O}^4$, is formed either by the action of bromine on phenol-phthalideïn, or by the oxidation of tetrabromophenol-phthalidin. It crystallises from alcohol in colourless opaque crystals, which melt above 280° ; dissolves in alkalis with yellow, and in strong sulphuric acid with blue colour. When heated to 140° with sulphuric acid, it behaves like tetrabromophenol-phthalideïn, yielding dibromoxanthraquinone. The *diacetyl-compound*, $\text{C}^{20}\text{H}^4(\text{C}^2\text{H}^3\text{O}^2)\text{Br}^4\text{O}^4$, formed by boiling it with acetic anhydride, melts at $182^\circ\text{--}183^\circ$.

Compounds of Phenol-phthalideïn with Phenols.—When a phenol is added to the solution of the phthalideïn in strong sulphuric acid, the colour of the solution at once changes from violet to blood-red, and on addition of water a red amorphous precipitate is thrown down. The compound with phenol is an amorphous brick-red powder, which dissolves with deep violet colour in alkalis, and is thrown down again by acids as a yellowish-red precipitate. Its alcoholic solution, when treated with bromine, yields a crystalline substitution-product, soluble with blue colour in alkalis. Tetrabromophenol-phthalideïn similarly combines with phenol, as does also phenol-phthalideïn chloride. The phenol-compound forms with ammonia at 150°–160° a crystalline substance soluble in alkalis, and with blue colour in strong sulphuric acid.

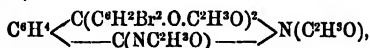
Phenol-hydroxy-phthaleïn, $C^{20}H^{14}O^5 = C^6H^3(OH) \left\langle \frac{C^6H^3(OH)^2}{CO} \right\rangle O$, a compound closely resembling phenol-phthaleïn, is formed by heating hydroxyphthalic anhydride with phenol and sulphuric acid, at 115° . It is somewhat more soluble in water than phenol-phthaleïn, and its dilute alkaline solution is rose-red. It is reduced by zinc-dust to a colourless hydroxyphthalin, which, by the action of concentrated sulphuric acid, is converted into a greenish-yellow hydroxyphthalidin; the latter, like the phthalidin, is oxidised by sulphuric acid and manganese peroxide in the cold, yielding a colourless hydroxyphthalideïn, which dissolves in sulphuric acid, with a blue violet colour (Baeyer, *Ber.* x. 1079).

$$\text{Diimidophenol-phthalein, } \text{C}^6\text{H}_4 \left\langle \begin{array}{c} \text{C}(\text{C}^6\text{H}_4\text{OH})_2 \\ \text{C}(\text{NH}) \end{array} \right\rangle \text{NH} \text{ (Baeyer u. Burkhardt, 1882)}$$

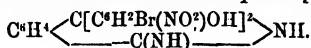
Ber. xi. 1297).—The ammonium salt of this compound is formed by heating phenolphthalein for three hours at 160°–170° with 10 pts. of aqueous ammonia; and on treating this salt with an acid, the free diimido-compound is obtained as a yellowish amorphous precipitate, which may be purified by treating its alcoholic solution with animal charcoal, and recrystallising it from a mixture of alcohol and benzene. It is somewhat soluble in boiling water, dissolves readily in alcohol, acetone, and glacial

acetic acid, sparingly in benzene and in chloroform, and crystallises in small colourless pointed needles melting at 265°–266°. It is dissolved by alkalis without coloration, by strong sulphuric acid, with yellow colour. Heated at 100° with strong hydrochloric acid, it is resolved into phenol-phthalein and ammonia.

Tetrabromodiimidophenol-phthalein, $C^6H^4 \begin{smallmatrix} \text{C}(C^6H^2Br^2OH)^2 \\ \text{C}(NH) \end{smallmatrix} NH$, prepared in like manner by heating tetrabromophenol-phthalein with 10 pts. aqueous ammonia for three hours at 160°–180°, melts at 280°, and is converted by acetic anhydride into the *tetracetyl-derivative*,

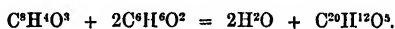


which melts at 241°. Tetrabromodiimidophenol-phthalein is converted by nitrous acid in alcoholic solution into *dibromodinitrodiimidophenol-phthalein*:



Resorcinol-phthalein, $C^{20}H^{14}O^8 = C^6H^4 \begin{smallmatrix} CO.C^6H^3(OH)^2 \\ CO.C^6H^2(OH)^2 \end{smallmatrix}$ and **Fluorescein**, $C^{20}H^{12}O^8 = C^6H^4 \begin{smallmatrix} CO.C^6H^3(OH) \\ CO.C^6H^3(OH) \end{smallmatrix} O$.

Fluorescein, the anhydride of resorcinol-phthalein, was discovered by Baeyer in 1871 (vii. 524); some of its derivatives were obtained by E. Fischer in 1874 (*Ber.* vii. 1211), and numerous others have more recently been prepared and examined by Baeyer (*Liebig's Annalen*, clxxxiii. 1). It is prepared by heating phthalic anhydride with resorcinol:



5 pts. of phthalic anhydride and 7 pts. of resorcinol are heated at 195°–200° till a solid mass is formed; this mass is boiled with water; and the undissolved portion is washed with alcohol, which dissolves resinous bye-products. The crude fluorescein thus obtained is dissolved in dilute soda-ley, precipitated with dilute sulphuric acid and extracted with ether. On adding a little absolute alcohol to this solution and distilling off the ether, fluorescein crystallises in grains or crusts. The crude fluorescein may also be purified by boiling it with a quantity of dilute soda which is insufficient to dissolve the whole, or by adding calcium chloride to its alkaline solution, filtering off the dark brown precipitate, and adding sodium phosphate, which produces a brown precipitate of calcium phosphate. The liquid is then again filtered and the pure compound precipitated from the filtrate by an acid.

Fluorescein is an amorphous, yellow, flocculent precipitate, which, on standing, heating, or drying, becomes crystalline, and consists of $C^{20}H^{12}O^8 + H^2O$. From alcohol it crystallises in dark red anhydrous grains, and from wood-spirit in yellow prisms, which probably contain methyl alcohol. It is almost insoluble in cold water, and dissolves sparingly in hot water with a yellow colour; in presence of acids it is more freely soluble. When freshly precipitated it dissolves readily in alcohol, ether, &c., but in the crystallised state only slowly, and after continued boiling. In hot acetic acid it is readily soluble, but nearly insoluble in benzene, toluene, and chloroform. The ethereal solution is pale yellow, and not fluorescent, whereas the yellowish-red alcoholic solution shows a green fluorescence. It may be heated to 280° without change, and begins to decompose at 290°. It dyes silk and wool yellow, but does not combine with mordants.

Fluorescein is a very weak acid, dissolving in strong alkalis with a dark red colour. This solution is not fluorescent, but changes on dilution to yellowish-red and yellow, and then exhibits a splendid yellowish-green fluorescence like that of uranium glass; and even if so much water is added that the liquid appears colourless in transmitted light, it shows in reflected light a green tinge like the colour of some Alpine lakes. The concentrated solution allows only the red and yellow rays to pass, whereas when dilute it gives an absorption-spectrum with a broad dark band in the green.

When alcoholic ammonia is added to a solution of fluorescein in ether, a reddish-yellow precipitate is formed, which loses ammonia on boiling or drying. In lime- and baryta-water fluorescein dissolves with a reddish-yellow colour; its alkaline solution is not precipitated by magnesium salts, while alum produces a reddish-yellow precipitate, which, on further addition of alum, becomes yellow, and then consists of pure fluorescein. The salts of some other heavy metals behave in a similar way; the lead and silver salts are more stable, and form reddish precipitates.

The striking colouring properties of fluorescein afford the means of detecting even

traces of resorcinol in presence of other phenols. It is only necessary to heat the substance with an excess of phthalic anhydride to near the boiling point of the latter. If the melt remains colourless, neither resorcinol nor pyrogallol or phloroglucol is present, but if it has a yellowish-red colour, these substances may be present. In the latter case the residue is dissolved in dilute soda, the smallest trace of resorcinol then becoming apparent by the fluorescence of the solution, while pyrogallol yields a blue, and phloroglucol a yellow liquid, which are not fluorescent. If a large proportion of pyrogallol should interfere with the reaction, a solution of potassium permanganate is carefully added, which destroys the gallein at once, but acts only slowly on the fluorescein.

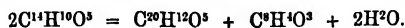
When fluorescein is heated with soda-ley and zinc-dust, the solution becomes colourless. On adding an acid and shaking with ether, *fluorescein* dissolves, and remains on evaporation as a colourless varnish. It forms an alkaline, colourless solution, which absorbs oxygen, while oxidising agents reconvert it quickly into fluorescein.

Fluorescein dissolves in concentrated sulphuric acid, with a dark red colour, a compound of the two bodies being formed, which is obtained pure by heating 2 mols. of resorcin and 1 of phthalic anhydride with an equal weight of sulphuric acid at 100° for five to six hours. The melt is washed with cold water and crystallised from wood-spirit at a low temperature. In this manner yellowish-red prisms are obtained, having the empirical formula $C^{20}H^{12}O^5 + SO^2$, and melting at 140°–150°. They are decomposed by recrystallisation, become turbid in damp air, and are resolved by warm water or alkalis into their components.

When fluorescein is boiled with sulphuric acid for some time, *resorcinol-coerulein* is formed, which is precipitated by water in dark red flakes. It dissolves in alkalis with a greenish blue, and in ether with a reddish-violet colour, and is also soluble in water, the concentrated solution being red, and the dilute splendid reddish violet. It is reduced in an alkaline solution by zinc-dust, and the red liquid thus formed again becomes blue on exposure to the air.

Resorcinol-phthalein, $C^{20}H^{14}O^6$, appears to be formed by the action of strong alkalis on fluorescein: for on boiling the latter with an excess of soda, the liquid, when sufficiently concentrated, becomes dark violet, and crystals of the same colour separate out. On adding water, the solution first becomes red, then assumes a dingy colour, and on standing, or more quickly on heating, it assumes the colour of an alkaline solution of fluorescein, which is precipitated on adding an acid. When alcohol is added to the violet solution, it becomes intensely violet, and then gives an absorption-spectrum having a dark band between the blue and green, and another between the green and red. If an acid be added to the violet alkaline solution, a yellow precipitate is formed, dissolving in ether with a yellow colour, and on then adding an alkali the latter becomes again violet. These reactions show that resorcin-phthalein is a stable body in presence of acids or strong alkalis, but that in a weak alkaline solution it soon changes again into its anhydride.

Monoresorcinol-phthalein, $C^{14}H^{10}O^5 = C^6H^4 \begin{matrix} \text{CO.C}^8H^6(OH)^2 \\ \text{COOH} \end{matrix}$, is formed by boiling fluorescein with an excess of caustic soda. The violet colour then changes to a brownish yellow, and on dissolving the melt in water, and adding an acid, a milky liquid is formed, from which crystals soon separate. These may be purified by crystallisation from dilute alcohol, and in this manner large yellowish striated crystals are obtained, which have the composition $C^{14}H^{10}O^5 + H^2O$, and give off their water at 100°. They melt at about 200°, but decompose even below this temperature when heated for some time. They dissolve sparingly in hot water, very freely in alcohol and ether, and form with alkalis a yellow solution, giving with silver nitrate a yellowish-white precipitate, which decomposes when heated, with separation of metallic silver. Monoresorcinol-phthalein, heated with resorcinol, yields fluorescein, which is also formed by heating it alone, phthalic anhydride subliming at the same time:



When somewhat strongly heated with soda, it is resolved into resorcinol and phthalic acid, which is further decomposed into carbon dioxide and benzoic acid.

Fluorescein-derivatives formed by replacement of Hydrogen in the Hydroxyl-groups.

Diacetyl-fluorescein, $C^{20}H^{10}O^5(C^2H^3O)^2$, is formed by heating fluorescein with four or five times its weight of acetic anhydride at 140°, until, on mixing a small quantity with alcohol, yellow crystals separate out, which are insoluble in ammonia. The whole is now treated in the same way, in order to convert the anhydride into the

acetic ether; the crystals are dissolved in acetic acid; and the solution is poured into several volumes of alcohol, whereupon the pure compound crystallises in colourless needles melting at 200° . It dissolves but sparingly in alcohol and wood-spirit, readily in acetic acid and hot acetone, but is insoluble in ether, benzene, and chloroform. It is decomposed into fluorescein and acetic acid by boiling alkalis, and rapidly in alcoholic solution; the same decomposition is produced by concentrated sulphuric acid and hot hydrochloric acid.

Dibenzoyl-fluorescein, $C^{20}H^{10}O^3(C^7H^5O)^2$, is obtained by heating fluorescein with benzoyl chloride for an hour at 140° . The dark brown residue is boiled with water and crystallised from acetone. It forms colourless crystals melting at 215° , dissolves sparingly in alcohol, wood-spirit, and ether, but readily in hot acetone. Alcoholic potash and concentrated sulphuric acid resolve it into its components.

Monethyl-fluorescein, $C^{20}H^{11}O^3(C^2H^5)$.—To prepare this compound, potash-solution is saturated with fluorescein, the liquid evaporated to dryness, and the residue heated for two or three hours at 120° with more than 2 mols. of ethyl bromide and ten times its weight of alcohol. The solution thus obtained is diluted with water and treated with sodium carbonate to remove unaltered fluorescein. The monethyl-compound is then extracted with ether, the solution evaporated, the residue dissolved in alcohol, and the solution concentrated. On heating the syrupy residue with ether, monethyl-fluorescein crystallises in pale yellow needles melting at 155° – 156° . It is readily soluble in alcohol, wood-spirit, chloroform, and benzene, and separates from these solvents as a syrupy mass, miscible with ether, and crystallising therefrom in needles, which are but sparingly soluble in the pure solvent. When water is added to a hot alcoholic solution, it becomes milky on cooling, and deposits turbid, yellow crystals. The compound is insoluble in dilute alkalis, which decompose it on heating. Concentrated sulphuric acid dissolves the ether with a greenish-yellow colour and a light green fluorescence, which disappears on adding water; on neutralising this solution, the unaltered compound is precipitated.

Diethyl-fluorescein, $C^{20}H^{12}O^3(C^2H_5)^2$, is not formed by the action of ethyl bromide on the potassium-compound, and only sparingly when the silver compound is heated with ethyl bromide and ten times its quantity of alcohol. The reddish-brown solution thus formed is concentrated and precipitated with water; the precipitate is treated with sodium carbonate to dissolve unaltered fluorescein; and the insoluble portion dissolved in ether, which is then evaporated, and the residue crystallised from alcohol, from which it separates in pale yellow plates. The compound is sparingly soluble in ether and alcohol; the alcoholic solution shows a vivid yellow fluorescence. It is not changed by dilute alkalis, but concentrated alkalis and sulphuric acid decompose it into alcohol and fluorescein.

Fluorescein chloride, $C^{20}H^{10}O^3Cl^2$, is easily obtained by heating 1 mol. fluorescein with 2 mols. phosphorus pentachloride for an hour or two to 100° . The product is successively treated with boiling water, a warm solution of sodium carbonate, and boiling alcohol. On dissolving the residue in hot toluene, and adding alcohol, the chloride crystallises out, and may be purified by repeating this operation. It forms colourless prisms melting at 252° , and dissolving readily in hot benzene, toluene, and chloroform, sparingly in alcohol, ether, acetic acid and chloroform. It is not changed by aqueous or alcoholic potash, while on fusing it with potash it is completely destroyed; but on heating it with slaked lime and a little water to 230° for some hours, it is again converted into fluorescein. Cold concentrated sulphuric acid dissolves it without alteration, but on boiling the solution, decomposition takes place, and on adding water, dark red flakes are precipitated, which dissolve in ether with a wine-red colour.

When the chloride is heated with an excess of fuming hydriodic acid to 150° for 5 or 6 hours, the iodide $C^{20}H^{12}O^3I^2$ is formed, crystallising from alcohol, ether, and acetic acid in small, rhombohedral plates, melting at 229° – 230° . It dissolves in dilute, but not in concentrated, alkalis.

Fluorescein-derivatives formed by replacement of Hydrogen in the Benzene-nuclei.

Dinitro-fluorescein, $C^{20}H^{10}(NO^2)^2O^3$, is obtained, but not quite pure, by dissolving fluorescein in 20 pts. of sulphuric acid and adding to the solution at 0° 2 pts. of fuming nitric acid. It is an amorphous yellow powder, dissolving in potash with a brown colour, which on heating changes to red and blue. On heating it with acetic anhydride, the compound $C^{20}H^8(NO^2)^2O^3(OCOCH^3)^2$ is formed, crystallising from alcohol in pale yellow needles. The same compound is formed by acting with nitric acid on a solution of acetylfluorescein in sulphuric acid, but not by dissolving it in cold nitric acid, while, on heating, tetranitrofluorescein is formed.

When dinitrofluoresceïn, or, better, its acetyl-compound, is boiled for five minutes with twenty times its weight of a lye containing 15 per cent. of alkali, the liquid changes to red and then blue. Acids produce a yellow precipitate, crystallising from ether-alcohol in glistening red crystals, consisting of $C^{20}H^{12}(NO^2)^2O^4$. This compound dissolves in alkalis with a blue colour, which on dilution first changes into violet and then again into blue. In its absorption-spectrum the yellow is completely cut off, and it shows a faint band between the blue and the green. The potassium salt of this *dinitro-fluoresceïn hydrate* appears to be formed by acting with alcoholic potash on dinitro-fluoresceïn, a blue crystalline body separating out, which is soluble in water.

Hydrochloric acid and tin reduce dinitro-fluoresceïn in alcoholic solution, diamido-fluoresceïn being probably formed. Its hydrochloride crystallises in greenish-grey needles, and dissolves in alkalis with a cherry-red colour. With nitrous acid it yields a body crystallising in yellow needles, and dissolving in alkalis with a light reddish-brown colour, and a strong dark green fluorescence.

Tetranitro-fluoresceïn, $C^{20}H^4(NO^2)^4O^5$, is formed by adding an excess of fuming nitric acid to about 5 grams of fluoresceïn; a violent reaction soon sets in, and as soon as the whole is dissolved, the compound may be precipitated with water, washed with water and a little alcohol, and dissolved in 50 pts. of boiling glacial acetic acid. On cooling, it separates in colourless, warty crystals. It is sparingly soluble in alcohol, with a yellowish-red colour and a faint yellowish-green fluorescence. The addition of a little mineral acid changes the colour into a pale reddish-violet, while on adding more, the liquid becomes colourless. In alkalis it dissolves with a yellowish-red colour, and in boiling water with a red colour. It dyes on wool an intense and fast orange. Dilute boiling alkalis do not change it, but concentrated alkalis change the colour to brown, and then to a pale yellow.

Tin and hydrochloric acid reduce tetranitrofluoresceïn to an amido-compound, dissolving in alkalis with a splendid bluish-violet-colour. In ammonium sulphide it dissolves with a brownish-red colour, which changes to violet on heating. Acids produce a brown precipitate, crystallising from ether in brown needles, and dyeing on silk a dingy violet.

Monobromofluoresceïn is formed by suspending fluoresceïn in 4 pts. of glacial acetic acid, and adding the required quantity of bromine mixed with 4 pts. of acetic acid. The compound is a yellowish-red amorphous body, which could not be obtained in crystals, and is changed by boiling acetic anhydride into a sticky mass. The alkaline solution has a reddish colour and faint green fluorescence.

Dibromofluoresceïn is formed by using 2 mols. of bromine. It forms compact reddish-brown needles with a deep green reflex, melts at 260° – 270° , and dissolves sparingly in acetic acid, alcohol, and acetic ether. Its alkaline solution is reddish-yellow, and shows a faint yellowish-green fluorescence. On boiling, the liquid changes into violet and blue, and the fluorescence into a dark green. On boiling it with acetic anhydride, the diacetyl-compound is formed, crystallising in colourless needles, which become red at 180° , and melt at 208° – 210° .

Dibromodinitrofluoresceïn, $C^{20}H^6Br^2(NO^2)^2O^5$, is formed by the action of nitric acid on dibromofluoresceïn or by that of bromine on dinitrofluoresceïn; also by dissolving 1 mol. of the tetranitro-compound in boiling acetic acid and adding 2 mols. bromine. It crystallises in compact yellow needles, which are very slightly soluble in alcohol and acetic acid, and dissolve in alkalis with a yellowish colour, changing to pale pink on addition of water. It is not fluorescent, but gives an absorption-spectrum resembling that of eosin. Its acetyl-derivative forms colourless needles which become violet at 210° and melts at 250° .

Tetrabromofluoresceïn, or *Eosin*, $C^{20}H^8Br^4O^5$.—This beautiful body, which is now manufactured on the large scale, and has been introduced into commerce by H. Caro as a dye-stuff, is formed by mixing fluoresceïn with 4 pts. of acetic acid, and adding the required quantity of bromine, which is diluted with four times its weight of acetic acid. It is also formed by adding bromine to a mixture of fluoresceïn and alcohol. It is purified by converting it into the pure potassium salt, and decomposing it by a mineral acid. An amorphous reddish-yellow precipitate is thus obtained, which is dried and dissolved in twenty times its weight of absolute alcohol, which is then distilled off until crystals begin to separate; or the potassium salt is decomposed by dilute sulphuric acid, and the liquid shaken with ether. The amorphous eosin is much more freely soluble than the crystals; the alcoholic solution is reddish-yellow and not fluorescent; it is but sparingly soluble in acetic acid, and almost insoluble in water, chloroform, and benzene. The crystals obtained from alcohol consist of $C^{20}H^8Br^4O^5 + C^2H^4O$, the alcohol being given off at 100° . If to a boiling alcoholic solution water is added until it becomes turbid, and then a little hydrochloric acid, the

liquid on boiling becomes clear again, and dull flesh-coloured crystals separate out, consisting of the pure compound.

Eosin is a bibasic acid; its salts are decomposed by mineral acids, but only imperfectly by acetic acid.

The *potassium salt*, $C^{20}H^6Br^1O^3K^2 + 6H^2O$, occurs in commerce as 'soluble eosin,' and forms brown, indistinct, prismatic crystals, with a blue and yellowish-green reflection. To obtain it in well-defined crystals, 100 pts. are dissolved in 50 pts. of water, and after addition of 100 pts. of alcohol and filtering, the solution deposits on standing splendid large plates, which in transmitted light appear red, and show the above reflection. They form a red powder, and belong to the triclinic system, being combinations of ∞P , $\infty \bar{P} \infty$, $\infty \bar{P} \infty$. They contain 5 mols. of water. On dissolving them in dilute alcohol, small reddish-brown crystals with a greenish-yellow reflex crystallise on cooling; they appear to contain 1 mol. alcohol. When the aqueous solution is quickly dried, the salt separates as a varnish having a yellowish-green metallic lustre. It dissolves in 2 pts. of water. The concentrated solution is dark yellowish-red, and in a thin layer pale pink. A dilute solution is yellowish-red, and exhibits a strong greenish-yellow fluorescence, which is also seen when the solution is very weak. Its absorption-spectrum has a broad dark band in the green. Its alcoholic solution exhibits similar colours, but a stronger fluorescence. The absorption-spectrum is destroyed by mineral acids, but not by acetic acid. A dilute aqueous solution containing 1 pt. in 150 gives the following reactions:

It is not changed by magnesium sulphate. Calcium and barium chloride give crystals on quickly boiling down the liquid, while cadmium sulphate deposits crystals in twelve hours, and nickel sulphate after weeks. Mercuric chloride gives at once a crystalline precipitate, and on standing a mixture of red and yellow crystals. Red amorphous precipitates are formed by salts of silver and lead, and reddish-brown by copper salts, while alum, zinc sulphate, stannous chloride, cobalt, nitrate, ferric and ferrous chloride, manganese sulphate, and bismuth nitrate, give amorphous reddish-yellow precipitates.

The *ammonium salt*, $C^{20}H^6Br^1O^3(NH^4)^2$, is obtained in small red needles, when a solution of tetrabromofluorescein in alcoholic ammonia is concentrated; they give off some ammonia on drying.

The *barium salt*, $C^{20}H^6Br^1O^3Ba + 2H^2O$, is prepared by mixing a solution of 2 pts. of the potassium salt with a solution of 1 pt. of barium chloride in such proportion that 60 pts. of water are present. On boiling, crystals separate out, of which more are obtained on evaporating the mother-liquor after cooling; they form small rhombic plates with a green reflex; the aqueous solution is yellowish-red, and shows a green fluorescence.

The *cupric salt*, $C^{20}H^6Br^1O^3Ca + \frac{1}{2}H^2O$, forms small yellowish-red needles, with a faint green lustre; it is more freely soluble than the barium salt.

The *cadmium salt* is deposited from a dilute solution in very glistening, small six-sided plates, having a brilliant greenish-yellow lustre; at 100° it loses water and becomes green.

The *silver salt*, $C^{20}H^6Br^1O^3Ag^2$, is a dark red precipitate, which is insoluble in salt-solutions, but dissolves in pure water and alcohol, and on heating it with the latter to 150° and leaving the solution to cool, it crystallises in microscopic, indistinct prisms, which are almost black. The precipitated salt becomes green when dried in a vacuum.

The *lead salt*, $C^{20}H^6Br^1O^3(PbOH)^2$, is obtained as a red precipitate, when the potassium salt is mixed with lead acetate, while the nitrate produces a similar precipitate which is not quite pure, $C^{20}H^6Br^1O^3Pb$.

Red Monethyl-tetrabromofluorescein or Erythrin, $C^{20}H^6Br^1O^3 \begin{Bmatrix} OC^2H^5 \\ OH \end{Bmatrix}$,

is formed when the potassium salt of eosin is heated at 140° – 150° for four or five hours with 15 pts. of alcohol and a quantity of potassium ethyl-sulphate, which would be sufficient to form the neutral ether. On cooling, the tubes are found to contain a gelatinous mass mixed with large crystals, which, on adding water, remain undissolved, while the unchanged potassium salt of eosin dissolves. The crystals, which consist of the potassium-compound of erythrin, are dissolved in alcohol of 50 per cent., and the solution mixed with acetic acid. If it be concentrated, erythrin separates as an amorphous precipitate, but from a dilute solution, it crystallises on evaporation in red needles with a beetle-green lustre. Erythrin is also formed, but not so readily, by the action of ethyl bromide on the potassium salt of eosin.

Erythrin dissolves slowly but freely in alcohol, with a reddish-yellow colour, and more readily in chloroform and acetic acid. From the first two solvents it separates in warty crystals, but when its solution in a mixture of acetic acid and alcohol is

diluted with water, distinct crystals are obtained. Erythrin heated with sulphuric acid to 150° is converted into eosin.

The *potassium salt*, $C^6H^3Br^4O^3(C^2H^3)K + H^2O$, is very sparingly soluble in water and absolute alcohol, but readily in hot, dilute alcohol of 50 per cent. The concentrated solution is yellowish-red, the dilute solution, pale pink, with a yellowish-green fluorescence; its absorption-spectrum is almost the same as that of eosin. The salt, called in commerce 'insoluble eosin,' dyes silk and wool like eosin, but the shades are more inclined to violet. The crystals appear to be rhombohedrons. They have a strong beetle-green lustre, and yield a pink powder. Silver nitrate precipitates the solution; the precipitate is amorphous, red in reflected light, and beautiful violet in transmitted light; it becomes crystalline on heating or standing, has a beetle-green lustre in the dry state, and appears deep blue in transmitted light. The lead salt is a similar precipitate.

Colourless Monethyl-tetrabromofluorescein.—This isomeride of erythrin is formed, together with the diethyl-compound, when the silver salt of eosin is heated with an excess of ethyl iodide or bromide, and twenty times its weight of alcohol at 100° for three to four hours. To separate the two ethers, the product is repeatedly exhausted with boiling alcohol, in which the monethyl-ether is more readily soluble and crystallises on cooling in yellow needles. As soon as the red crystals of the diethyl-ether appear, the treatment with alcohol is stopped, and the yellow crystals are boiled with a solution of potash in alcohol of 50 per cent., which dissolves chiefly the monethyl-compound. The solution is then mixed with more dilute alcohol and acetic acid, and the ether which separates out is again treated in the same way, and is thus obtained in colourless needles. It is sparingly soluble in boiling alcohol, and a little more freely in glacial acetic acid; its very pale solution is coloured light yellow by alkalis, and gives yellowish-white precipitates with silver nitrate and lead acetate. It dissolves but sparingly in carbonates and dilute alkalis. The existence of two isomeric monethyl-compounds shows that the two hydroxyls occupy different positions.

Diethyl-tetrabromofluorescein, $C^{20}H^6Br^4O^3(C^2H^5)^2$, is obtained not only as described above, but also by heating the silver salt of the red monethyl-ether with ethyl iodide. To isolate it from the residue from the preparation of the white monethyl ether, this residue is exhausted with chloroform, and the crystals, after boiling with dilute alcoholic potash, are recrystallised from chloroform. It forms small but well-defined crystals, which appear to be rhombohedrons, and dissolve very sparingly in alcohol and ether, with a yellowish colour, and freely in chloroform and glacial acetic acid, with a reddish-yellow colour. Aqueous alkalis do not decompose it on boiling, but alcoholic potash, as well as hot sulphuric acid, converts it into eosin.

Monomethyl-tetrabromofluorescein, or *Methylerythrin*, $C^{20}H^7Br^4O^3(CH^3)$, is sparingly soluble in alcohol, more freely in chloroform, and crystallises in red needles, having a beetle-green lustre.

Acetyl-tetrabromofluorescein is formed by heating eosin with three times its weight of acetic anhydride to 140° . It forms colourless needles dissolving sparingly in alcohol, acetone, wood-spirit, and acetic ether, and more freely in hot benzene and chloroform. On heating, it becomes red at 180° , but melts only at 278° .

Tetrabromofluorescein chloride, $C^{20}H^6Br^4O^3Cl^2$, is obtained by heating tetrabromofluorescein with phosphorus pentachloride for an hour at 100° . The product, after being well boiled with water and a dilute alkali, is dissolved in seventy times its weight of concentrated sulphuric acid at 150° , filtered through asbestos, and then mixed with 3 vols. of alcohol. The liquid is then heated to the boiling point, and water added, until crystals begin to separate out. It forms colourless needles, which melt and sublime without decomposition; its only solvent is concentrated sulphuric acid, which decomposes it only at the boiling point.

When tetrabromofluorescein is heated with concentrated potash on a water-bath, the liquid soon assumes a blue colour, and shows, when diluted, a very strong, dark-green fluorescence. The dilute solution turns red in contact with the air, but the concentrated solution remains blue. Mineral acids produce a pale reddish-yellow precipitate of the hydrate $C^{20}H^6Br^4O^3 + H^2O$, which has undoubtedly a constitution analogous to that of the dinitro-compound. When the solution is heated on a water-bath, the blue colour changes to dark yellow, more quickly if the potassium salt is heated with twenty times its weight of soda of 50 per cent. Mineral acids precipitate the solution.

Dibromomonoresorcinol-phthalein, $C^{18}H^4 \begin{Bmatrix} CO \cdot C^6HBr^2(OH)^2 \\ CO \cdot H \end{Bmatrix}$, crystallises in small, colourless, rhombic plates, which melt at 218° – 220° . It is almost insoluble in

water, and dissolves in alkalis and alcohol with a yellow colour. On fusing it with resorcinol, dibromofluoresceïn seems to be formed, and when it is heated with phenol and sulphuric acid at 120° , a body is formed, dissolving in alkalis with a red colour.

The acid liquid from which the preceding compound has been precipitated contains *dibromoresorcinol*, $C^6H^2Br^2(OH)^2$, which is shaken out with ether. It crystallises from warm water in colourless needles, melting at 92° – 93° ; the aqueous solution gives, with ferric chloride, first a violet colour, which soon changes into an indistinct dirty green.

Water and sodium-amalgam, or zinc-dust and soda, reduce tetrabromofluoresceïn to fluoresceïn, and when the tetrabromo-compound is boiled for five minutes with twenty times its weight of concentrated sulphuric acid, *heptabromocæruleïn*, $C^{10}H^{13}Br^7O^4$, is formed, which, by adding water, is precipitated as a dark violet mass, and during washing, begins to dissolve with a blue colour. On dissolving it in dilute potash, and adding alcoholic potash, a dark-blue precipitate of the potassium-salt is obtained, which yields, with acids, the pure cæruleïn, readily soluble in acetone, from which it crystallises in steel-blue needles. The absorption-spectrum of the dilute solution shows a faint broad band in the green, and the dilute alkaline solution, which has a greenish-blue colour, gives an absorption-band in the red.

Quinol-phthaleïn, $C^{20}H^{12}O^3$. *Hydroquinone-phthaleïn*.—This compound, isomeric with fluoresceïn, and therefore, properly speaking, the anhydride of quinol-phthaleïn, $C^{20}H^{14}O^4$, was discovered by Grimm (*Ber.* vi. 576), who obtained it, together with quinizarin, by heating a mixture of quinol and phthalic anhydride with strong sulphuric acid. According to Ekstrand, however (*ibid.* xi. 713), it is better to use zinc-chloride as the dehydrating agent, the yield of the phthaleïn being then 70 per cent. of the quinol used, whereas with sulphuric acid it is only 25 per cent. The best proportions are 2 mols. quinol, 1 mol. phthalic anhydride, and a quantity of zinc chloride equal to thirteen times the weight of the mixture, the whole being heated at 120° – 130° for twelve to fourteen hours:



The product is boiled with water to remove the stannic chloride, unaltered quinol, and phthalic anhydride; it is at first viscid, but ultimately becomes crystalline. To purify it, the crystalline residue is dissolved in alcohol, and boiled for a long time with animal charcoal, the filtrate, which is cloudy at first, gradually solidifying to a felted mass of needles. Pure quinol-phthaleïn is colourless, and melts at 226° – 227° (uncorr.) (Ekstrand): at 233° – 234° (Grimm). It dissolves but slightly in hot water, and separates on cooling in small tabular crystals; easily in wood-spirit, alcohol, acetic acid, and acetone; also in ether, from which it separates in long needles on evaporation. It is but sparingly soluble in chloroform or benzene even when hot, and not at all in light petroleum. The needles which separate from the alcoholic solution contain 1 mol. alcohol; if, however, the alcoholic solution is diluted with much water, needles are precipitated, which on boiling are converted into thin plates containing 1 mol. of water instead of alcohol. From the ease with which the alcohol and water replace one another, it is probable that the latter is present as water of crystallisation, and does not go to the formation of hydroxyl-groups so as to produce a tetrahydroxyl-compound; and that this is confirmed by the fact that this water is easily driven off below 160° , and that the hydrated and dehydrated products are perfectly similar in their properties; moreover, it has not been found possible to obtain a triacetyl-derivative of this body. A solution of quinol-phthaleïn mixed with an alkali acquires a deep violet colour, which becomes brown and muddy on standing. In sulphuric or hydrochloric acid, quinol-phthaleïn dissolves to a red liquid, and the latter acid gives a crystalline compound, corresponding probably with the hydrochloride of orcin-phthaleïn, but it has not yet been investigated.

Diacetyl-quinol-phthaleïn, $C^{20}H^{10}(C^2H^3O)^2O^5$, obtained by heating the phthaleïn with acetic anhydride for two or three hours, forms colourless crystals melting at 210° .

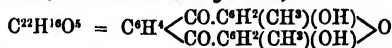
Bromo-compounds.—When a solution of the phthaleïn in alcohol or acetic acid is acted on by bromine, the mixture left at rest, and then diluted with water, a yellow flocculent precipitate is obtained, soluble in dilute alcohol, but it has not yet been obtained in crystalline form.

Pentabromo-quinol-phthaleïn, $C^{20}H^7Br^5O^3$, is obtained as a yellow crystalline precipitate when an excess of bromine is added to an acetic acid solution of the phthaleïn, and the mixture boiled for a long time. The pure compound is a colourless crystalline powder (m. p. over 300°), insoluble in acetic acid, but easily soluble in nitrobenzene, from which it separates in small tables. It gives a colourless solution with alkalis.

Quinol-phthalin, $C^{20}H^{14}O^5$, is obtained when the phthalein is heated for four hours with zinc-dust and soda-solution. It crystallises from benzene in large colourless tables (m. p. 202° uncorr.), containing 1 mol. benzene; dissolves to a colourless solution in alkalis, and to a red liquid in sulphuric acid, the solution when diluted with water giving an olive-green flocculent precipitate of quinol-phthalidin, which dissolves in ether with a green fluorescence; the ethereal solution, however, soon oxidises, with production of a dark violet powder. Quinol-phthalin does not combine with hydrochloric acid.

Diacetyl-phthalin, $C^{20}H^{12}(C^2H^3O)^2O^5$, is obtained by boiling the phthalin for two hours with an excess of acetic anhydride. It crystallises in colourless prisms (m. p. 190° uncorr.), and dissolves in wood-spirit much more easily than diacetyl-phthalein. At first it is not acted on by alkalis, but gives a violet coloration on gentle warming.

Orcinol-phthalein, or rather its **Anhydride**,



(F. Fischer, *Ber.* vii. 1214; *Liebig's Annalen*, clxxxiii. 63). This compound is prepared by heating 3 pts. phthalic anhydride, 5 pts. distilled orcinol, and 5 pts. strong sulphuric acid at 135° for about two hours. At this temperature, the reaction goes on smoothly and without evolution of sulphur dioxide, whereas at lower temperatures that gas is given off in considerable quantity. By dissolving the melt in dilute potash-ley, boiling the solution, precipitating with acetic acid, and recrystallising the precipitate from acetone, the compound is obtained in colourless needles mostly united in forked groups. It is insoluble in water, ether, benzene, and toluene, but dissolves readily in alcohol, wood-spirit, acetone, and hot glacial acetic acid, and is precipitated from the last-mentioned solution by water in white flocks. Alkalis dissolve it with dark red colour. It is decomposed by heat. On boiling it with strong sulphuric acid and mixing the resulting solution with water, dark brown flocks are thrown down, consisting of a body which dissolves in ammonia with dark brown colour, and is precipitated by baryta in the form of a black lake.

Monacetyl-orcinol-phthalein is obtained by prolonged boiling of the phthalein with glacial acetic acid. The *diacetyl-derivative*, $C^{22}H^{14}(C^2H^3O)^2O^5$, formed by treating the phthalein with 3 or 4 pts. of acetic anhydride, crystallises from alcohol in white slender needles, melting at 219° – 220° , insoluble in water, ether, and benzene, sparingly soluble in alcohol and wood-spirit, more freely in acetone; easily resolved into its constituents by alkalis and concentrated acids.

Orcinol-phthalein unites with *mineral acids*, forming dark-red unstable compounds, among which the *hydrochloride*, $C^{22}H^{16}O^5.HCl$, is most readily obtained pure, and separates from an alcoholic solution of the phthalein mixed with strong hydrochloric acid in dark red flocks, which give off their hydrochloric acid on exposure to the air, even at ordinary temperatures, and more quickly when heated or boiled with water.

When bromine is added to a solution of the phthalein in boiling acetic acid, the *tetrabromo-compound* is formed, while in a cold alcoholic solution the *pentabromo-compound* is produced. Both these compounds are pale yellow powders, nearly insoluble in all solvents.

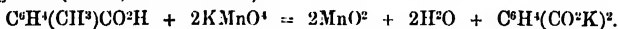
Orcinol-phthalin, $C^{22}H^{20}O^5$, is formed by the action of zinc-dust on a solution of the phthalein in dilute soda-ley, the red liquid becoming colourless and yielding, on addition of sulphuric acid, white flakes of the phthalin, which when heated in the air are reoxidised to the phthalein. Its *diacetyl-compound*, $C^{22}H^{18}(C^2H^3O)^2O^5$, formed by heating it with acetic anhydride, is much more stable, and crystallises from benzene in cubes melting at 211° .

PHTHALEIN DYES. F. Reverdin (*Monit. scient.* [3], vii. 860) has obtained a yellow dye-stuff, called *chrysolin*, by the action of sulphuric acid on a mixture of phthalic acid and benzyl-resorcinol (formed by the action of benzyl chloride on resorcinol, *q. v.*), or by first heating 460 grams of sulphuric acid and 1 kilo. of phthalic acid in a retort placed in an oil-bath at 130° – 140° , whereby phthalic anhydride is produced, then adding 1 kilo. of resorcinol, 460 grams of sulphuric acid, and 1 kilo. of benzyl chloride, and heating the whole gently over a water-bath. When no more hydrochloric acid is evolved, the reaction is completed by heating for twelve hours in the oil-bath at 135° – 145° . The whole is then left to cool, and the solid mass is broken up and dissolved in dilute caustic soda at the boiling point. When the residue no longer diminishes, the solution is filtered, and the acid colouring matter is precipitated by means of hydrochloric acid, washed with cold water, dissolved in a quantity of sodium carbonate sufficient to saturate the acid, and evaporated to dryness. The sodium salt of benzylated fluorescein constitutes chrysolin. This substance forms a

mass with green metallic reflex, and yields a red-brown powder. It is soluble in water and alkalis, the solutions being precipitated by acids in yellow flocks. It yields bromated, iodated, and nitro-derivatives, which are all fine colouring matters. It may be fixed directly upon silk and wool. The latter takes the dye better when mordanted with lead acetate and alum. Cotton is mordanted with sulphate of alumina and dyed at a hand-heat. The shade of chrysolin approaches that of turmeric; it resists the action of light well. Similar colouring matters are produced by the action of the chlorides of fatty hydrocarbons on resorcinol. Methyl-resorcinol prepared by heating sodium resorcinate in alcoholic solution with methyl chloride under pressure likewise yields a yellow dye-stuff when treated as above.

Bouchardt a. Girard (*Monit. scient.* [3], vii. 985) have also obtained colouring matters by the introduction of alcohol-residues into resorcinol and the phthaleins. For this purpose, phenols and diphenols are heated to 120°–150° with diatomic acids, e.g. oxalic, lactic, camphoric, phthalic acids, &c.; the products are subjected to the action of solutions of alkaline hypochlorites or hypobromites; and the resulting colouring matters are precipitated from the alkaline solutions by acids. Thus when fluorescein, produced by heating a mixture of 1.4 kg. resorcinol with 1 kg. phthalic anhydride to 200°, is dissolved in a small quantity of soda-ley, and gradually mixed with 56 litres (per 1 kg. fluorescein) of a solution of sodium hypochlorite (sp. gr. 1.4), a colouring matter, called 'Aureosin,' is obtained, which, when separated by an acid, exhibits a greenish-yellow dichroism in reflected light and a red colour in transmitted light. Silk dyed with it fluoresces like the solution. This aureosin, treated at boiling heat with nitric acid diluted with 2 vols. water, is converted into another dye-stuff, called 'Rubeosin,' which dissolves in alkaline liquids with deep red colour, and dyes silk scarlet. If alkaline hypobromites are used instead of hypochlorites, the resulting colouring matters exhibit a somewhat more yellowish tint. Similar dye-stuffs are obtained by the action of sodium or potassium acetate in presence of acetic acid upon eosin, the reaction being completed, at 200°–250°, within three or four hours. The product analogous to aureosin is converted by oxidation into a body analogous to rubeosin. Phthalins may also be oxidised by hypochlorites or hypobromites in presence of cobalt-salts, and the process stopped at any required point. The bodies obtained by the action of alcoholic bromides and iodides on aureosin and rubeosin are likewise dye-stuffs. Lastly, products resembling aureosin are formed by oxidising fluorescein with mixtures of bromates or chlorates with hydrochloric or hydrobromic acid respectively.

PHTHALIC ACIDS, $C^6H^4O^4 = C^6H^4(CO^2H)^2$. (1). ORTHOPHTHALIC, or simply PHTHALIC ACID [1 : 2], is formed by oxidation of orthotoluic acid with potassium permanganate (Weith, *Ber.* vii. 1057):

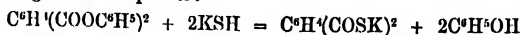


Synthetically it may be formed by combination of carbon monoxide with salicylic acid and with resorcinol. From *salicylic acid* it is produced by heating that substance with a mixture of sulphuric acid and potassium ferrocyanide, and when the reaction is ended, treating the resulting mass with ether, which extracts the phthalic acid, or by heating a mixture of sulphuric acid and formic acid with salicylic acid until gas is no longer disengaged. The mass is exhausted with ether, which on evaporation yields perfectly pure phthalic acid. *Resorcinol* combines readily with carbon monoxide to form phthalic acid, but as an excess of resorcinol is always present, the phthalic acid unites with it and forms fluorescein. When salicylic acid or resorcinol is heated with oxalic acid and sulphuric acid, that is to say, with a mixture yielding carbon dioxide and monoxide simultaneously, neither phthalic acid nor fluorescein is formed; but when salicylic acid or resorcinol is heated with a mixture of oxalic acid and glycerol, that is, with a mixture yielding carbon dioxide in the first phase of the operation and carbon monoxide in the second, carbon dioxide is disengaged freely, and phthalic acid or fluorescein appears as soon as the mixture yields carbon monoxide (A. Guyard, *Bull. Soc. Chim.* [2], xxix. 247).

Preparation from Naphthalene.—The following modification of Deponville's process for obtaining phthalic acid by the action of potassium chlorate and hydrochloric acid on naphthalene (*Compt. rend.* lvi. 82; *Jahresb. f. Chem.* 1865, 399) is recommended by C. Häussermann (*Dingl. pol. J.* cccxiii. 310). A mixture of 1 pt. naphthalene and 2 pts. potassium chlorate is added by successive small portions to a five-fold quantity of ordinary hydrochloric acid; the product is well washed with lukewarm water, then dried, and digested at a gentle heat with petroleum-benzin; and the resulting mass, consisting chiefly of naphthalene tetrachloride, is heated with five or six times the quantity of nitric acid of specific gravity not exceeding 1.35, till the liquid is perfectly homogeneous. On expelling the excess of acid, and leaving the liquid to cool, phthalic acid crystallises out in quantity equivalent to 30 per cent. of phthalic anhydride.

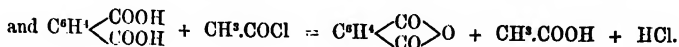
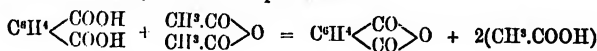
Phthalic acid is also formed from *nitronaphthol* (m. p. 128°) by repeated treatment with nitric acid and evaporation (Liebermann, *Ber.* viii. 689).

Phenyl Phthalate, $C^6H^4(COOC^6H^5)^2$, is prepared by heating phthalic chloride with the calculated quantity of phenol as long as hydrochloric acid continues to be evolved, and crystallising the product from hot alcohol. It forms groups of small colourless prisms, melts at 60°, and distills without alteration. Nitric acid attacks it violently, forming dinitrophenol and nitrophthalic acid. A hot alcoholic solution of the ether treated with potassium hydrosulphide yields the potassium salt of thio-phthalic acid together with phenol:



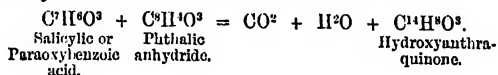
(J. Schroder, *Ber.* vii. 704).

Phthalic Anhydride, $C^6H^4O^3 = C^6H^4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, is produced by the action of acetic anhydride or acetyl chloride on phthalic acid:



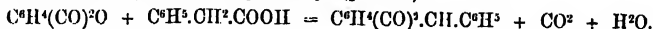
It melts at 127°. The anhydrides of succinic, diphenic, and other bibasic acids may be prepared by similar reactions (Anschütz, *Ber.* x. 1881).

Phthalic anhydride heated with *phenols* in presence of dehydrating agents (sulphuric acid, zinc chloride, &c.), produces phthaleins (pp. 1603–1613). On gently heating it with ordinary phenol and sulphuric acid, the liquid assumes a yellowish-red colour, and phenol-phthalein, $C^{20}H^{14}O^4$, is formed, which, on further addition of sulphuric acid, is converted, without change of colour, into phenol-phthalein-sulphonic acid. On increasing the heat, the yellow-red colour changes to dark red and ultimately to brown-yellow, and the liquid, on addition of water, deposits flocks of monoxanthraquinone, $C^{14}H^8O^3$ (p. 99). The formation of this latter body is not essentially dependent on the previous formation of phenol-phthalein, but may take place directly from phenol. A similar result is obtained when the phenol is replaced by phenolsulphonic acid, phenoldisulphonic acid, oxysulphobenzide, anisole, anisic acid, or salicylic acid:

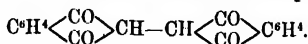


(Bayer a. Caro, *Ber.* vii. 968).

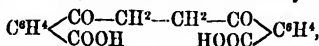
Phthalic anhydride, heated with *acetic* and *propionic anhydrides* in presence of the sodium salts of the respective acids, yields phthalyl-acetic and phthalyl-propionic acids respectively (pp. 1621, 1622). Heated with *phenylacetic* (*α-toluic*) acid, it yields benzylidene-diphthalyl (p. 1621):



When phthalic anhydride is heated with *succinic acid* and sodium acetate, the mixture being kept in a state of fusion as long as it continues to give off carbon dioxide, a residue is obtained which, after crystallisation from nitrobenzene, consists of ethineorthophenylene-diketone or ethine-diphthalyl:

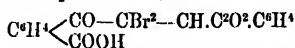


This compound crystallises in yellow needles, melting above 350°. When boiled with dilute potash-ley, it dissolves slowly, and the solution yields with hydrochloric acid a precipitate of phenylene-ethylene-ketone carboxylic acid (p. 1561):



formed from ethine-diphthalyl by assumption of 2 mols. water.

When ethine-diphthalyl dissolved in acetic acid is heated with *bromine* at 100° in a sealed tube, two atoms of hydrogen are replaced by bromine and a molecule of water is taken up, producing the compound



which is decomposed by heating with alkalis (Gabriel a. Michael, *Ber.* x. 1559).

(2). **META- or ISOPHTHALIC ACID**, $[\text{CO}^2 : \text{CO}^2\text{H} = 1 : 3]$, is produced: α . Together with metabromobenzoic acid, by the action of ethyl-chlorocarbonate and sodium-amalgam on metadibromobenzene (Wurster, p. 163). β . By fusing potassium benzoate with potassium formate (Meyer, p. 259). γ . By heating the nitril of disulphobenzoic acid, $\text{C}^6\text{H}_4\text{CO}^2\text{H}\cdot\text{SO}^2\text{H}\cdot\text{H}\cdot\text{SO}^2\text{H}\cdot\text{H}^2$, or that of benzenedisulphonic acid $[1 : 3]$ with alcoholic potash (p. 251). δ . By oxidation of meta-toluic acid (Weith a. Landolt, *Ber.* viii. 715). ϵ . By prolonged boiling with nitric acid of the products obtained by the action of hydrochloric acid on resorcinol (Barth a. Weidel, *Ber.* x. 1464). ζ . By oxidation of colophony with nitric acid (Schreder, *Lieb. Ann.* clxxii. 93).

Phenyl Isophthalate crystallises in long slender needles melting at 120° (Schreder, *Ber.* vii. 704).

(3). **PARAPHTHALIC or TEREPHTHALIC ACID** $[1 : 4]$ is formed: α . By heating sodium parasulphobenzoate with sodium formate, and, together with isophthalic acid, by heating sodium benzoate to the point of carbonisation (p. 260). β . By heating the nitril of benzeneparadisulphonic acid with alcoholic potash (p. 250). γ . Together with terebic acid, by oxidation of turpentine-oil with nitric acid of sp. gr. 1.4, diluted with 2 vols. water (Schreder, *Ber.* vii. 794). This is the process by which terephthalic acid was first obtained (v. 725). W. C. Williams, however (*Ber.* vi. 1094), by oxidising turpentine-oil with nitric acid of sp. gr. 1.25, obtained only terebic acid without a trace of terephthalic acid. δ . Together with paratoluic acid, by the action of nitric acid on the portion of Eucalyptus oil boiling between 172° and 175° (Homeyer, *Arch. Pharm.* [3], v. 326). ϵ . By oxidation of curcumin with chromic acid mixture (Gajevsky, *Ber.* vi. 196).

Ethers. *Propyl Terephthalate*, $\text{C}^6\text{H}^4(\text{CO}^2\text{C}^3\text{H}^7)^2$, obtained by heating silver terephthalate mixed with two or three times its weight of sand, with propyl iodide, crystallises in white needles an inch long, dissolves easily in hot alcohol and in ether, and melts at 31° . *Pseudopropyl terephthalate*, prepared in like manner, crystallises in shining white laminae, melting at 55° – 56° , and exhibiting the same relations of solubility as the normal propyl-ether. *Isobutyl terephthalate*, $\text{C}^6\text{H}^4(\text{CO}^2\text{C}^4\text{H}^9)^2$, is best prepared from terephthalyl chloride and isobutyl alcohol, and crystallises in dazzling white needles having a fatty lustre, melting at 52.5° , easily soluble in ether. The normal butyl ether has not been obtained in crystalline form (J. Berger, *Ber.* x. 1742). *Phenyl terephthalate*, prepared by heating terephthalyl chloride with phenol, forms long slender needles melting at 120° (Schreder, *ibid.* vii. 704).

Homoterephthalic acid, $\text{C}^6\text{H}^4\text{O}^4 = \text{C}^6\text{H}^4 \begin{smallmatrix} \text{COOH} \\ \diagup \\ \text{COOH} \end{smallmatrix}$, is formed, together with propyl-benzoic acid, by oxidation of propyl-benzene (*q.v.*) with dilute nitric acid. It is a faintly yellowish powder, which sublims without fusing, is nearly insoluble in all solvents, and forms a silver salt, $\text{C}^6\text{H}^4\text{O}^4\text{Ag}^2$, and a barium salt, $\text{C}^6\text{H}^4\text{O}^4\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ (Paternò a. Spica, *Gazz. chim. ital.* 1877, 361).

Hydroxyphthalic Acids, $\text{C}^6\text{H}^3(\text{OH})(\text{COOH})^2$, syn. with **PHENOL-DICARBOXYLIC ACIDS** (pp. 1531–1534).

Nitrophthalic Acids, $\text{C}^6\text{H}^3(\text{NO}^2)(\text{COOH})^2$. The prismatic nitrophthalic acid, melting at 212° , which Faust obtained by digesting *o*-phthalic acid with a mixture of nitric and sulphuric acids (vii. 978), is also formed, together with the corresponding aldehyde (m. p. 135°), by oxidising nitronaphthalene in acetic acid solution with chromic acid. It is decomposed by hydrobromic acid, with formation of carbon dioxide and di- and tri-bromobenzoic acids. Hydriodic acid converts it into metamidobenzoic acid (Beilstein a. Kurbatow, *Ber.* xii. 688).

According to Faust, this acid is reduced by tin and hydrochloric acid to metamidobenzoic acid, with evolution of carbon dioxide. According to O. Miller, on the other hand (*Ber.* xi. 1191), the reduction is not attended with evolution of carbon dioxide, but yields a tin-salt, $\text{C}^6\text{H}^3(\text{NH}^2)(\text{COOH})^2\cdot\text{HCl}\cdot\text{SnCl}^2 + 2\text{H}_2\text{O}$, which separates in nearly colourless needles, crystallises from aqueous solution in light brown rhombic plates and needles, but from dilute hydrochloric acid in crystals of the original form and colour. The formation of the hydrochloride of metamidobenzoic acid takes place only when the solution, after being freed from tin by hydrogen sulphide, is concentrated by evaporation.

Amidophthalic acid.—The ethylic ether of this acid is prepared by mixing a solution of ethyl nitrophthalate (obtained by the action of hydrochloric acid on a hot solution of the nitronaphthalic acid above described) in 2 vols. of alcohol, with 10 vols. of hydrochloric acid, of sp. gr. 1.09; the mixture being kept cool by means of ice, and zinc-dust added gradually, till the oily drops disappear and a distinct evolution of gas takes place. The liquid is then diluted with water and nearly neutralised with sodium carbonate, and sodium acetate is added, whereupon ethyl amidophthalate

crystallises out. This product crystallises from ether in large, colourless, monoclinic prisms, agreeing in composition with the formula $C^6H^4(NH^2)(COOC^2H^3)^2$. It dissolves in hydrochloric acid without alteration, and is precipitated from the solution by alkalis or by sodium acetate (W. Königs, *Ber.* x. 124).

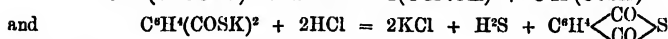
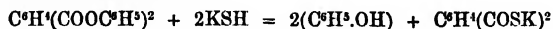
Isonitrophthalic acid (m. p. 160°) (O. Miller, *Ber.* xi. 393, 992, 1191).—This acid is formed, together with the preceding nitro-acid, by heating phthalic acid on the water-bath with a mixture of nitric and sulphuric acids. The two nitro-acids are produced in nearly equal quantities, and after they have been precipitated by water, the filtered liquid is found to contain picric and acetic acids, with a very small quantity of formic acid. The ordinary prismatic nitro-acid is easily separated by repeatedly crystallising the crude nitro-product from water; but the isonitrophthalic acid, which is more soluble, crystallises in needles, and forms a compound with picric acid, is more difficult to separate. The separation may, however, be effected by picking out the needle-shaped crystals, converting them into the sparingly soluble barium salt, and decomposing this salt with hydrochloric acid. The isonitro-acid thus obtained forms pale yellow slender needles very easily soluble in water, alcohol, and ether, insoluble in benzene; it melts at 160°, and is resolved at 165° into water and the anhydride.

The *barium salt*, $C^6H^3(NO^2)(CO^2)^2Ba + 2H^2O$, is a light yellow precipitate made up of microscopic laminae. The *silver salt*, $C^6H^3(NO^2)(CO^2Ag)^2$, is thrown down by silver nitrate from a solution of the acid neutralised with ammonia, as a whitish precipitate, sparingly soluble in pure water, but very soluble in ammoniacal water, and separating from this solution in long colourless needles.

Normal Ethyl Isonitrophthalate, $C^6H^4(NO^2)(CO^2C^2H^3)^2$, is formed, together with very small quantities of the acid ether, on saturating the alcoholic solution of the acid with hydrochloric acid. It is liquid at first, but afterwards solidifies to a crystalline mass which melts at 32°. By reduction, it yields *ethyl isoamidophthalate*, $C^6H_5(NH^2)(CO^2C^2H^3)^2$, which crystallises from alcohol in short prisms of considerable size.

When isonitrophthalic acid is reduced by tin and hydrochloric acid, the resulting tin-salt does not separate out like that which is obtained from the prismatic nitro-acid; ultimately, however, metamidobenzoic acid is formed in this as in the former case.

Thiophthalic Acid, $C^6H^4 \begin{smallmatrix} \text{COSH} \\ \text{COOH} \end{smallmatrix}$ [1 : 2] (Schreder, *Ber.* vii. 704). The potassium salt of this acid is obtained by dissolving potassium sulphhydrate (2 mols.) in a hot alcoholic solution of 1 mol. phenyl phthalate (p. 1614), whereupon the liquid turns red. After the reaction has continued for a quarter of an hour, ether is added, which precipitates part of the resulting potassium thiophthalate in the form of a red oil. The greater part of the colourless liquid decanted therefrom is distilled off; and the remainder is diluted with water—whereby phenol is precipitated—and after removal of the latter, acidulated with hydrochloric acid. The thiophthalic acid thereby separated in slender needles is purified by distillation, whereby a colourless oil is obtained which immediately solidifies; the last traces of free sulphur, however, can be removed from it only by fusion with finely divided silver or with mercury. The substance thus purified crystallises from alcohol in long brittle needles having the composition of thiophthalic anhydride, $C^6H^4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} S$. Its formation is represented by the following equations:



Thio-isophthalic acid, [1 : 3].—The potassium salt of this acid is formed in like manner by the action of KHS on phenyl isophthalate, and is thrown down from the resulting solution by ether in yellow needles, which when decomposed by hydrochloric acid yield thio-isophthalic acid in the form of an oil (Schreder).

Thioterephthalic acid, [1 : 4].—The potassium salt, prepared in like manner, separates on addition of ether in the form of a red mud. The acid separated therefrom after purification a white amorphous powder not volatile without decomposition (Schreder).

PHTHALIC ALCOHOL, $C^6H^4O^2 = C^6H^4(CH^2OH)^2$ (Hessert, *Ber.* xii. 646). This alcohol, produced by the action of sodium-amalgam on phthalic chloride, is a crystalline body, soluble in water, alcohol, and ether, melting gradually at 56°–62°. It is oxidised by potassium permanganate to phthalic acid, by nitric acid to phthalide, and is distinguished from the latter compound, which it otherwise resembles, by the

action of sulphuric acid, this reagent dissolving it with a red colour, and rapidly converting it into resinous products. On reduction by boiling it with hydriodic acid and phosphorus, it yields orthoxylene. It acts readily on acetic and benzoic chlorides. The *acetate*, $C^6H^4(CH^3.OO^2C^2H^3O)^2$, is a crystalline body (m. p. 37°) which may be distilled without decomposition, and is converted by the action of hydrochloric acid gas into the chloride $C^6H^4(CH^2Cl)^2$, which when heated with lead nitrate and water yields phthalide (p. 1618).

PHTHALIC ALDEHYDES, $C^6H^4O^2 = C^6H^4(COH)^2$. The compound hitherto regarded as orthophthalic aldehyde (vi. 943) appears from recent investigations by Hessert to have the constitution of an anhydride, $C^6H^4 \begin{smallmatrix} CH^2 \\ CO \end{smallmatrix} O$. See PHTHALIDE (p. 1618).

Terephthalic Aldehyde, $C^6H^4(COH)^2$ [1 : 4], is prepared by boiling tolylene chloride, $C^6H^4Cl^2$, with 20 pts. water and 1 pt. lead nitrate till nitrous acid is no longer given off, and distilling the mixture, the aldehyde then passing over, though not readily, with the vapour of water. When purified by crystallisation from boiling water, it forms white slender needles which melt at 114° – 116° , dissolve with moderate facility in ether, very easily in alcohol, very slightly in cold water, and in about 60 pts. of boiling water; it dissolves also at 40° – 50° in 20–25 pts. of a saturated solution of acid sodium sulphite, but the resulting compound has not been obtained in the solid state. By oxidation with potassium dichromate and sulphuric acid, it yields terephthalic acid. By mixing its alcoholic solution with an alcoholic solution of potassium cyanide, it is converted into an amorphous yellowish substance which melts at 170° – 174° , is insoluble in water and in ether, somewhat soluble in boiling alcohol, soluble in alkalis but not in alkaline carbonates, and appears to be a polymeride of terephthalic aldehyde (Grimaux, *Compt. rend.* lxxxiii. 825).

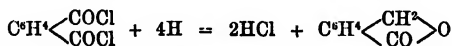
The tolylene chloride obtained from coal-tar xylene is accompanied by a liquid chloride, which, when treated as above, yields needles melting at 88° , and probably consisting of *isophthalic aldehyde* (Grimaux).

PHTHALIC CHLORIDES, $C^6H^4(COCl)^2$. *Orthophthalic chloride* acts upon dimethylaniline, producing dimethylaniline-phthalein (p. 1310), and in like manner on other tertiary bases, e.g. on methyldiphenylamino (O. Fischer, *Ber.* ix. 1753).

Isophthalic chloride is obtained by heating isophthalic acid with phosphorus pentachloride. The mixture liquefies, and on distilling it after the evolution of hydrochloric acid has ceased, the chloride is obtained as an oil which boils at 276° , and quickly solidifies. After rectification it is nearly inodorous and melts at 41° .

Terephthalic chloride has a pungent, cinnamon-like odour, melts at 78° , and boils at a temperature too high to be exactly determined (Schreder, *Ber.* vii. 704).

PHTHALIDE, $C^6H^4O^2 = C^6H^4 \begin{smallmatrix} CH^2 \\ CO \end{smallmatrix} O$ (Baeyer a. Hessert, *Ber.* x. 123; Hessert, *ibid.* x. 1445; xi. 637). This compound, hitherto regarded as orthophthalic aldehyde, $C^6H^4(COH)^2$, is formed by the action of nascent hydrogen on phthalic chloride:



According to Hessert, it is best prepared by a modification of Kolbe a. Wischin's process (vi. 943), namely by the action of zinc and hydrochloric acid on an *etheral solution* of phthalic chloride. Metallic zinc is covered with a solution of phthalic chloride (8 to 10 grams) in ether (400 c.c.), and dilute hydrochloric acid is gradually added, the liquid being kept cool at the beginning; afterwards, however, the action goes on more slowly, and stronger hydrochloric acid may be used. The solution of zinc chloride which forms must be removed from time to time, so that the zinc may always project into the ethereal liquid. After about twelve hours, the ethereal solution is distilled off; the phthalide which remains is digested with water to remove undecomposed chloride; ammonium carbonate added in excess; and the product again extracted with ether. On subsequently distilling off the ether, the phthalide remains as a mass which solidifies in the crystalline state, and may be purified by recrystallisation from water.

Pure phthalide melts at 73° . When heated at 180° – 200° with *hydriodic acid* (b. p. 127°) and *red phosphorus*, it is completely resolved into a mixture of hydrocarbons boiling between 112° and 120° , and intermediate in composition between toluene and xylene. By *potassium permanganate* in alkaline solution it is easily oxidised to phthalic acid. When its warm aqueous solution is mixed with a concentrated solution of *acid sodium sulphite*, the liquid solidifies after some time to a mass of long silky needles, which were supposed by Kolbe a. Wischin (vi. 493) to consist

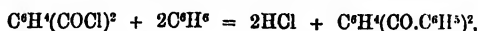
of a compound of phthalic aldehyde with the acid sodium sulphite. Hessert, however, finds that they do not contain a trace of this salt, but consist of the pure compound $C^8H^4O^2$, which therefore appears to be incapable of uniting with acid sulphites of alkali-metal, and accordingly cannot be regarded as an aldehyde. On this account, and in accordance with the reactions about to be described, Hessert assigns to it the constitutional formula above given.

Alkalis and alkaline carbonates, at the boiling heat, convert phthalide into an acid, $C^8H^4O^3 = C^8H^4 \begin{smallmatrix} \text{CH}^2\text{OH} \\ \text{COOH} \end{smallmatrix}$, called benzene-ortho-alcoholic acid (originally called *phthaldehydic acid*), metameric with hydroxytoluic acid, $C^8H^8(CH^3)(OH)CO^2H$, which separates from the cooled solution on acidulation as a white powder. This acid is much less soluble in cold water than phthalide, but dissolves readily in alcohol and ether. It melts at 118° , giving off 1 mol. H^2O and being reconverted into phthalide. The same change takes place on boiling it with water. It is a well-characterised monobasic acid, reddens litmus strongly, and dissolves with effervescence in alkaline carbonates. Its salts are all soluble in water; those of the alkaline earths dissolve in the smallest quantities of water and alcohol, without however being deliquescent. The *silver salt*, prepared with recently precipitated silver oxide, crystallises from the aqueous solution in small octohedrons; its solution decomposes when heated. The *lead salt* is decomposed by water. Aqueous ammonia gradually dissolves phthalide, producing *ammonium benzene-o-alcoholate*; alcoholic and ethereal solutions of ammonia do not act upon phthalide, even at 220° . At 240° , however, the ethereal solution of ammonia gives rise to a new body which is nearly insoluble in water, alcohol, ether, and carbon sulphide, but dissolves in glacial acetic acid at boiling heat, and crystallises therefrom in slender needles which do not melt at 260° .

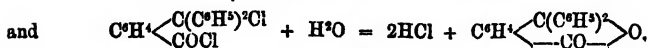
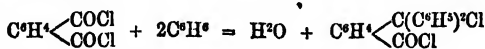
Aniline acts on phthalide at a temperature above its boiling point, converting it into the compound $C^8H^4 \begin{smallmatrix} \text{CH}^2 \\ \text{CO} \end{smallmatrix} N.C^6H^5$. The two substances are heated together in a sealed tube at 200° – 220° for some hours; and the product is precipitated by dilute hydrochloric acid, washed with water, and crystallised from hot alcohol, from which it separates in silvery laminae melting at 160° . It is very sparingly soluble in boiling water, somewhat more freely in ether, easily in chloroform. It is decomposed by boiling with concentrated alkalis or acids. By oxidation it is converted into phthalidanil, $C^8H^4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} N.C^6H^5$, or phthalanilic acid.

Sodium-amalgam converts phthalide in aqueous or alcoholic solution chiefly into hydrophthalide, $C^8H^4 \begin{smallmatrix} \text{CH}^2 \\ \text{CHOH} \end{smallmatrix} O$, which is obtained as a viscid mass, very easily soluble in all solvents except water, gradually becoming solid when dried over sulphuric acid, and horny at a gentle heat. Potassium permanganate oxidises it to phthalic acid. Together with the hydrophthalide there is also formed a small quantity (about 10 per cent.) of a body having the composition $C^{10}H^{10}O^4$, which crystallises from alcohol in fine white needles melting at 197° , soluble in water and alcohol, sparingly in ether, insoluble in chloroform. By oxidation with potassium permanganate it yields phthalic acid and diphtalic acid, $C^{10}H^{10}O^6$ (vii. 980), whence it appears to consist of phthalylpinacene, $C^8H^4 \begin{smallmatrix} \text{CH}^2\text{OH} & \text{HOH}^2\text{C} \\ \text{CHOH} & \text{—HOHC} \end{smallmatrix} C^8H^4$ (Hessert).

Diphenyl-phthalide, $C^{20}H^{14}O^2 = C^8H^4 \begin{smallmatrix} \text{C}(C^6H^5)^2 \\ \text{CO} \end{smallmatrix} O$. This compound, formerly called *phthalophenone*, was discovered by Friedel and Crafts (*Revue scientifique*, 2 Mars, 1878), who obtained it by heating phthalic chloride with benzene in presence of aluminium chloride, and represented its formation by the equation



analogous to that which expresses the formation of diphenyl ketone (benzophenone) from benzoyl chloride and benzene. But according to Baeyer (*Ber.* xii. 642), the aluminium chloride acts, not upon the chlorine, but on the oxygen-atom of one of the groups $COCl$, giving rise to its replacement by $2C^6H^5$, the reaction taking place by two stages as follows:



On the conversion of this compound into phenol-phthalein, see PHTHALEINS (p. 1603).

Benzyl-phthalide, $C^{14}H^{12}O^2 = C^6H^4 \left\langle \begin{smallmatrix} CH.CH^2.C^6H^5 \\ CO \end{smallmatrix} \right\rangle O$, is formed by the action of sodium-amalgam on deoxybenzoin-carboxylic acid (p. 1620). It crystallises in long colourless needles, melts at 56° – 57° , dissolves in alcohol, ether, and hot alkalis, but is insoluble in water (Michael a. Gabriel, *Ber.* xi. 1620).

PHTHALIDEIN (PHENOL), $C^{20}H^{14}O^4$, and **PHTHALIDIN**, $C^{20}H^{14}O^3$. See PHTHALEINS (pp. 1604, 1605).

PHTHALIMIDE, $C^8H^5NO^2 = C^6H^4 \left\langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \right\rangle NH$. This compound, originally obtained by heating phthalate or phthalamate of ammonium (iv. 632), is also produced, together with carbon dioxide and ammonia, by fusing phthalic anhydride with urea, and, with evolution of phosgene gas, by the action of phthalic chloride on urea. It melts at 228° – 229° (R. Biedermann, *Ber.* x. 1166).

Ethyl-phthalimide, $C^{10}H^9NO^2 = C^6H^4(CO)^2N(C^2H^5)$, obtained by distilling phthalic anhydride with aqueous ethylamine, forms white needles melting at 78° – 79° . *Tri-bromomethyl-phthalimide*, obtained, together with the dibromo-derivative, by the action of bromine on ethyl-phthalimide, crystallises in truncated prisms, which melt with decomposition at 186° – 188° . It is insoluble in water, slightly soluble in hot alcohol, decomposed by hot aqueous potash into hydrogen bromide and a basic compound (A. Michael, *Ber.* x. 1644).

Phenyl-phthalimide, or *Phthalanil*, $C^{14}H^9NO^2 = C^6H^4(CO)^2N(C^6H^5)$.—This body, obtained by melting phthalic acid with aniline, has been already described (iv. 632). It is also formed by limited oxidation of the compound $C^6H^4 \left\langle \begin{smallmatrix} CH^2 \\ CO \end{smallmatrix} \right\rangle N(C^6H^5)$, produced by the action of aniline on phthalide (p. 1619), and is converted by further oxidation into phthalanilic acid, $C^6H^4 \left\langle \begin{smallmatrix} CO.NH.C^6H^5 \\ COOH \end{smallmatrix} \right\rangle$ (iv. 628).

Substituted Phthalanils are obtained by melting phthalic anhydride in excess with substituted anilines, as long as water continues to be given off, boiling the pulverised melt with water to remove the excess of phthalic acid, and recrystallising the product from an appropriate solvent.

p-Chlorophenyl-phthalimide, $C^6H^4(CO)^2N.C^6H^4Cl$, prepared from *p*-chloraniline and phthalic anhydride, crystallises from boiling alcohol in long slender silky needles, melting at 194° – 195° , easily soluble in hot alcohol, benzene, and glacial acetic acid, less soluble in ether.

p-Bromophenylphthalimide, $C^6H^4(CO)^2N.C^6H^4Br$, from bromaniline (m. p. 65°). Crystallises from an alcoholic solution in scales or needles, which melt at 203° . *p-Iodophenylphthalimide*, prepared from *p*-iodaniline (m. p. 60°), forms needle-shaped crystals melting at 227° , soluble in benzene and in glacial acetic acid.

m-Nitrophenylphthalimide, $C^6H^4(CO)^2N.C^6H^4(NO^2)$, obtained from *m*-nitraniline (m. p. 110°) is deposited from boiling acetic acid in colourless needles melting at 242° (S. Gabriel, *Ber.* xi. 2260).

m-Diphtalimidodibromodiphenyl, $[C^6H^4(CO)^2N]^2C^{12}H^6Br^2$, obtained in like manner from phthalic anhydride and dibromobenzidine, separates from boiling glacial acetic acid in groups of slender crystals, is nearly insoluble in alcohol, ether, and benzene, and melts at 300° – 301° .

Diphtalimidodiphenyl, similarly prepared from benzidine, crystallises in yellow scales, very sparingly soluble, and melting at a very high temperature (Gabriel).

Paratolylphthalimide, $C^{13}H^{11}NO^2 = C^6H^4(CO)^2N(C^6H^4.CH^3)$, is obtained by fusing together phthalic acid and paratoluidine in molecular proportions, and distilling the product. It crystallises from alcohol in needles, melts at 200° , is nearly insoluble in boiling water and in cold alcohol, but soluble in hot alcohol, and can be sublimed. On account of its sparing solubility it is but very slowly oxidised by potassium permanganate, the product consisting of *hydroxyphthalyl-paramidobenzoic acid*, $C^6H^4 \left\langle \begin{smallmatrix} CO.NH.C^6H^4.COOH \\ COOH \end{smallmatrix} \right\rangle$, which is also nearly insoluble in water, melts with decomposition at 275° – 277° , and is converted by heating with hydrochloric acid into paramidobenzoic acid (Michael, *Ber.* x. 576).

PHTHALIMIDOBENZOIC ACID, $C^6H^4(CO)^2N.C^6H^4.COOH$. The *ortho*-compound is obtained by fusing phthalic anhydride with anthranilic acid, and separates on cooling from the solution of the product in boiling water, in broad yellowish prisms melting at 217° , easily soluble in ether, benzene, and glacial acetic acid. Its

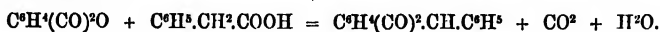
silver salt is a white pulverulent precipitate. The *meta-acid*, prepared in like manner, forms spherical groups of crystals or capillary needles melting at 275.5° – 276° , soluble in hot glacial acetic acid, less soluble in benzene and in ether. Its *silver salt*, $C^6H^4(CO)^2N.C^6H^4.CO^2Ag$, separates from a hot solution in radio-fibrous groups of needle-shaped crystals (Gabriel, *loc. cit.*)

PHTHALOPHENONE, $C^{20}H^{14}O^2$. Syn. with Diphenyl-phthalide (p. 1619).

PHTHALYL (DI-), $C^6H^4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C^6H^4$. This compound, formed by the action of finely-divided silver on phthalic chloride, has been already described (vii. 979).

Ethine-diphthalyl, or *Ethine-orthophenylene-diketone*, $C^{18}H^{10}O^4 = C^6H^4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CH-CH \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C^6H^4$, obtained by heating phthalic anhydride with succinic acid in presence of sodium acetate, is described under PHENYLENE KETONES (p. 1561 of this volume).

Benzylidene-diphthalyl, $C^{18}H^{10}O^2 = C^6H^4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CH.C^6H^5$, is formed, with evolution of CO^2 , by heating phthalic anhydride with phenylacetic (α -toluic) acid and sodium acetate:

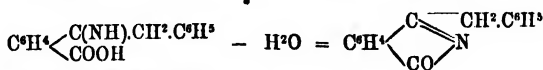
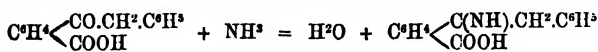


It is insoluble in hot water and in dilute ammonia, but dissolves in boiling alcohol, and in hot aqueous ammonia or potash solution. On the addition of an acid to its solution in caustic alkali, *ortho-deoxybenzoincarboxylic acid*, $COOH.C^6H^4.CO.CH^2.C^6H^5$, separates in the liquid state, but solidifies when left at rest for several hours. This acid when pure is soluble in alcohol, and is deposited from a boiling aqueous solution in long shining prisms (m. p. 74° – 75°) containing 1 mol. of water of crystallisation, which is expelled at 50° . The silver salt, $C^{15}H^{13}AgO^4$, is indistinctly crystalline. The acid heated to 190° with hydriodic acid is converted into *ortho-dibenzylcarboxylic acid*, $COOH.C^6H^4.CH^2.CH^2.C^6H^5$, which is deposited from its solution in alcohol in large tabular crystals, insoluble in water, but readily soluble in alkalis. The aqueous solution of ammonium ortho-dibenzylcarboxylate forms a white precipitate with lead and silver salts, pale blue with copper salts. The silver salt when gently heated yields dibenzyl, $C^6H^5.CH^2.CH^2.C^6H^5$.

Ortho-deoxybenzoincarboxylic acid is converted by sodium-amalgam into benzyl-phthalide, $C^6H^4 \begin{smallmatrix} \diagup CH-CH^2-C^6H^5 \\ \diagdown CO \diagup \end{smallmatrix}$ (Michael a. Gabriel, *Ber.* xi. 1018).

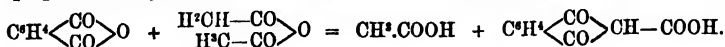
Imido-deoxybenzoincarboxylic Anhydride, $C^{15}H^{11}NO = C^6H^4 \begin{smallmatrix} \diagup C=CH^2.C^6H^5 \\ \diagdown CO \diagup N \end{smallmatrix}$, is

formed by the action of ammonia at 100° on deoxybenzoincarboxylic acid, and separates, on recrystallising the resinous residue thereby produced from alcohol, in yellow scales melting at 182° – 183° , insoluble in hot water, not affected either by alkaline or by acid solutions. Its formation appears to take place by two stages, thus:



(Gabriel a. Michael, *Ber.* xi. 1679).

PHTHALYLACETIC ACID, $C^{10}H^6O^4 = C^6H^4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{smallmatrix} CH-COOH$ (Michael a. Gabriel, *Ber.* x. 391, 1551, 2199). This acid is prepared by boiling a mixture of 1 pt. phthalic anhydride, 2 pts. acetic anhydride, and 0.2 pt. dry sodium acetate:



After the boiling has been continued for two hours, two-thirds of the quantity of acetic anhydride added is to be distilled off, and the residue mixed with four or five times its volume of glacial acetic acid, whereupon the phthalylacetic acid separates out, and may be obtained in colourless needles by crystallisation from glacial acetic acid or nitrobenzene. When the process is thus conducted, the yield amounts to 14 per cent. of the phthalic anhydride used; but if the boiling be continued for more

than two hours, large quantities of resin are formed, and the yield of phthalylacetic acid is greatly diminished.

Reactions.—1. A neutral solution of phthalylacetic acid in *potash* yields, on addition of hydrochloric acid, a precipitate of the unaltered acid; a solution containing excess of potash, on the other hand, gives no immediate precipitate with hydrochloric acid, but the acidulated liquid, if left at rest, gradually deposits a new acid, $C^6H^4O^6$, containing the elements of 1 mol. phthalylacetic acid and 2 mols. water. This acid is bibasic, and has the constitution of benzacet-ortho-carboxylic acid $C^6H^4 \begin{smallmatrix} \text{CO.CH}^2\text{COOH} \\ \text{COOH} \end{smallmatrix} + H^2O$. When boiled in aqueous or alkaline solution, or when fused, it gives off water and carbon dioxide, and is converted into acetophenone-*o*-carboxylic acid, $C^6H^4 \begin{smallmatrix} \text{CO.CH}^3 \\ \text{COOH} \end{smallmatrix}$. This last acid, which may also be produced directly by heating phthalylacetic acid with water to 200° , forms crystals having a vitreous lustre, a sweet taste, and melting at 114° – 115° . Its salts are difficult to crystallise.

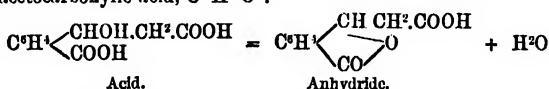
2. The action of *bromine* on phthalylacetic acid dissolved in acetic acid gives rise to tribromacetophenone-*o*-carboxylic acid, $Br^3C.CO.C^6H^4.COOH$, which melts at 159.5° – 160° , and is resolved by alkalis into bromoform and phthalic acid. When, on the other hand, bromine acts upon dry phthalylacetic acid in presence of chloroform, the mixture being heated for two hours at 100° in a sealed tube, phthalylmonobromacetic acid, $C^6H^4(CO)CBr.COOH$, is formed, which melts at 232° – 235° , and is easily decomposed by alkalis and water at 180° . 3. *Chlorine* acts on phthalylacetic acid suspended in glacial acetic acid in the same manner as bromine, converting it into trichloracetophenone-*o*-carboxylic acid, which melts at 144° . 4. *Ammonia* converts it into phthalylacetamide.

5. Phthalylacetic acid, heated on the water-bath with strong *sulphuric acid*, is converted, with separation of carbon dioxide and water, into a yellow body, C^6H^4O , which is also formed in small quantity in the preparation of phthalylacetic acid. This compound, when fused with potash, is converted into an acid body having the empirical formula $C^6H^4O^2 = C^6H^4O + H^2O$, which crystallises in colourless prisms, dissolves easily in alcohol, ether, glacial acetic acid, and alkalis, but only sparingly in benzene and carbon disulphide. Heated to low redness with lime, it yields triphenylbenzene, $C^6H^3(C^6H^5)^3$. This reaction shows that the acid in question must be a polymeride of $C^6H^4O^2$, and that it is in fact *phenenyl-tribenzoic acid*, $C^6H^3(C^6H^4.COOH)^3$. On this view, the formation of triphenylbenzene from it will be represented by the equation

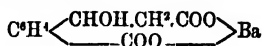


(Michael a. Gabriel, *Ber.* xi. 1007).

6. *Sodium-amalgam* converts phthalylacetic acid in alkaline solution into a monobasic acid, $C^6H^4O^4$ (m. p. 150°), which may be regarded as the anhydride of benzhydrylacetocarboxylic acid, $C^6H^4O^5$:



Benzhydrylacetocarboxylic acid is not known in the free state, but some of its salts have been prepared. The *barium salt*



gives off $\frac{1}{2}$ mol. water at 100° . When heated to 220° – 240° , it gives off, in addition to its water of crystallisation, a second molecule of water, and its solution, acidulated with hydrochloric acid, then yields a pulverulent precipitate of a bibasic acid, isomeric with the anhydride $C^6H^4O^4$. The group $CH(OH)CH^2COOH$ is thereby converted into $CH=CH-COOH + H^2O$, and the new acid is *cinnamocarboxylic acid*,

$C^6H^4 \begin{smallmatrix} \text{CH=CH-COOH} \\ \text{COOH} \end{smallmatrix}$, which takes up 2 at. bromine, forming the dibromide, $C^6H^4 \begin{smallmatrix} \text{CHBr.CHBr.COOH} \\ \text{COOH} \end{smallmatrix}$, and unites with nascent hydrogen, forming hydro-cinnamocarboxylic acid, $C^6H^4 \begin{smallmatrix} \text{CH}^2\text{CH}^2\text{COOH} \\ \text{COOH} \end{smallmatrix}$.

PHTHALYLPROPIONIC ACID, $C^6H^4O^4 = C^6H^4 \begin{smallmatrix} \text{CO} \\ \diagdown \quad \diagup \\ & \text{CO} \end{smallmatrix} \text{CH.CH}^2\text{COOH}$

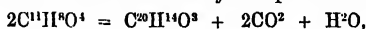
(Gabriel a. Michael, *Ber.* xi. 1017, 1679). This acid is prepared by heating a mixture of phthalic and propionic anhydrides with sodium propionate, dissolving the product in boiling acetic acid, and filtering the liquid while hot. On cooling, the acid separates in slender needles melting at 245° – 248° .

Phthalyl-propionamide, $C^8H^4(CO)^2.CH.CH^2.CONH^2$, separates in iridescent scales melting at 193° – 195° , on adding an acid to a hot solution of phthalylpropionic acid in ammonia.

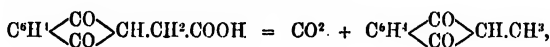
Propiophenone-carboxylic acid, $C^8H^4\begin{smallmatrix} CO.C^2H^3 \\ COOH \end{smallmatrix}$, is formed when phthalylpropionic acid is boiled with excess of potash-solution: $C^{11}H^{10}O^4 + H^2O = C^{10}H^{10}O^3 + CO^2$, and crystallises from its alcoholic solution in slender colourless needles, which melt at 91° – 92° . The silver salt, $C^{10}H^9AgO^3$, also forms long needle-shaped crystals.

Phthalylpropionic acid is converted, by the action of *phosphorus* and *strong hydriodic acid*, into propylbenzoic acid, $COCH.C^6H^4.CH^2.CH^2.CH^3$; thus: $C^{11}H^{10}O^4 + H^4 = C^{10}H^{12}O^2 + CO^2$. This compound, which is easily soluble in the usual solvents, forms crystalline scales melting at 58° .

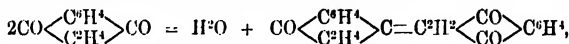
The action of strong *sulphuric acid* on phthalylpropionic acid at the heat of the water-bath is similar to that, which it exerts on phthalylacetic acid (p. 1621), giving rise to the compound $C^{20}H^{14}O^3$, which crystallises from alcohol in silky needles, melts at 235° – 237° , is insoluble in acids and aqueous alkalis, and appears to yield an acid by fusion with potash. Its formation may be represented by the equation:



and the reaction may resolve itself into two stages, the first consisting in the formation of the diketone, phthalylethylidene, thus:



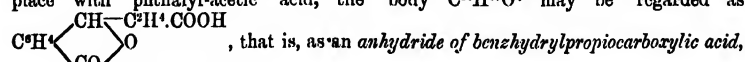
two molecules of which then unite together under the influence of the sulphuric acid, with elimination of a molecule of water



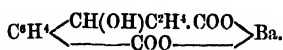
the change being similar to that which takes place in the conversion of acetone, C^3H^6O , into mesityl oxide, C^6H^8O .

Phthalylpropionic acid, dissolved in dilute *soda-ley*, is converted by assumption of water into benzoylpropionic acid, $C^{11}H^{10}O^3 = C^8H^4\begin{smallmatrix} CO.C^2H^3.CO^2H \\ CO^2H \end{smallmatrix}$.

This acid has not been isolated, but its formation may be inferred from the action of sodium-amalgam on the alkaline solution just mentioned, whereby a body is formed which crystallises from dilute alcohol in shining colourless needles having the composition $C^{11}H^{10}O^4$. This last compound is slightly soluble in cold, moderately soluble in hot water, and dissolves readily in the other ordinary solvents; it softens at 135° , melts at 140° , dissolves in aqueous alkalis, decomposes carbonates, and is converted by boiling with baryta-water into a barium salt having the composition $C^{11}H^{10}BaO^5$. From these properties, and from the analogy of the reaction to that which takes place with phthalyl-acetic acid, the body $C^{11}H^{10}O^4$ may be regarded as



$C^8H^4\begin{smallmatrix} CH(OH).C^2H^3.COOH \\ COOH \end{smallmatrix}$. The constitution of the barium salt may be represented by the formula:



PHYCOCYANOGEN and **PHYCOERYTHRIN**. See PLANT-COLOURS.

PHYLLIC ACID. A substance obtained by C. Bongarel (*Bull. Soc. Chim.* [2], xxviii. 148) from the leaves of several trees, *e.g.* the cherry-laurel, quince, apple, peach, almond, mulberry, and elder. It is found in the alcoholic extract of the leaves, and, after purification, forms colourless crystalline granules, soluble in alcohol, ether, chloroform, and carbon bisulphide, insoluble in water. Sp. gr. about 1.014. It melts at 170° , and solidifies on cooling in flat prisms terminated by pyramids of about 120° . When heated above 180° it decomposes, giving off white fumes of balsamic odour, which condense in oily drops. Dilute acids have no effect upon it. In contact with cold potash, it does not apparently dissolve, but combines slowly, forming a body which crystallises in prismatic needles with square base. These needles, which are

the potassium salt of phyllic acid, are slightly soluble in cold water, soluble in hot slightly alkaline solutions; insoluble in strong alkalis; soluble in alcohol, ether, and chloroform. The analysis of the acid led to the formula $C^{22}H^{40}O^{18}$, which, however, requires confirmation. Both the acid and its salts are optically dextrogyrate.

PHYLLITE- or SERICITE-GNEISS. A rock occurring in the Casanna Pass, in the Engadine, Switzerland, examined by C. W. Gümbel (*Jahrb. f. Min.* 1878, 383; *Chem. Soc. J.* xxxii. 207).

PHYLLOCYANIC ACID, PHYLLOCHROMOGEN, PHYLLO-ANTHIN. See CHLOROPHYLL (p. 452).

PHYSOSTIGMINE. According to Hesse (*Jahresh. f. Chem.* 1877, 177), this base, the active principle of the Calabar bean (iv. 635), is amorphous. The bean, however, yields also a substance (m. p. 133° – 134°) very much like cholesterolin and isocholesterin, and this is probably the substance which was mistaken by Vee (*J. Pharm.* [4], i. 70) for a crystalline alkaloid (the so-called 'eserine') of the Calabar bean. The base described by Petit (vii. 472) under the name of *escrine* was doubtless identical with physostigmine.

PHYTOSTERIN, $C^{26}H^{40}O$ (Hesse, *Liebig's Annalen*, xcii. 175). A neutral substance, identical or homologous with cholesterolin, obtained from Calabar beans by extraction with petroleum-ether. The resulting solution leaves on evaporation an oily residue, which after some time solidifies to a butyraceous mass of crystals; and on pressing this mass between bibulous paper to remove the oil, dissolving the residue in hot alcohol, and recrystallising from ether and alcohol successively, brilliant colourless tabular crystals are obtained which melt at 132° – 133° , and give on analysis numbers agreeing with the formula $C^{26}H^{40}O.H^{2}O$. By recrystallisation from petroleum ether, this substance is obtained in anhydrous needles.

A solution of phytosterin in chloroform shows left-handed polarisation, $(\alpha)_D = -34.2^{\circ}$ at 15° . Phytosterin seems to be identical with Kolbe's 'cholesterin obtained from peas.'

Cholesterolin, obtained from gall-stones, crystallises from alcohol and from chloroform in forms the same as those assumed by phytosterin, but the crystals obtained from an ethereal solution consist for the most part of tables. Cholesterolin melts at 145° – 146° . Dehydrated cholesterolin in chloroform solution gave a left-handed polarisation, $(\alpha)_D = -(36.61 + 0.249 p)$.

Cholesterolin, according to all chemists who have hitherto examined it, has the same composition as that which Hesse assigns to anhydrous phytosterin, viz. $C^{26}H^{40}O$ (i. 924; vi. 446; vii. 328; viii. 454). Hesse, however, is inclined to regard it as the next lower homologue of phytosterin, viz. $C^{25}H^{38}O$; he thinks it probable, also, that the two substances occur together in the animal organism.

PICOLINE, C^8H^7N . See PYRIDINE-BASES.

PICOTITE. This black chromiferous spinel, originally found as a constituent of Lherzolite (iv. 640), occurs also in the basalt nodules of Kasakov. Two analyses by F. Farsky (*Verh. geol. Reichsanst.* 1876, 207) gave the following results:

SiO^2	Al^2O^3	Cr^2O^3	MgO	FeO
3.77	50.34	5.75	17.87	22.27 = 100
1.25	52.47	7.01	18.23	21.42 = 100.38

PICRACONITINE. A base isomeric with aconitine, sometimes occurring, together with the latter, in the root of *Aconitum Napellus*. It is amorphous, and exhibits but little physiological activity (C. R. A. Wright, *Chem. Soc. J.* xxxi. 243).

PICRAMIDE, or *Trinitraniline*, $C^6H^2(NO^2)^3NH^2 = C^6.NH^2.NO^2.H.NO^2.H.NO^2$ (p. 210). This compound, heated with alcoholic ammonium sulphide at 130° , is converted into a dinitrodiphenylene-diamine, melting at 210° – 211° (p. 1558).

Picramide unites with aromatic hydrocarbons and amines, forming crystalline compounds. The *benzene-compound*, $C^6H^2(NO^2)^3NH^2.C^6H^6$, separates from a solution of picramide in benzene, on slow evaporation, in pale yellow transparent prisms which fall to pieces on exposure to the air. A similar compound, crystallising in brown transparent needles, is formed with *toluene*.

The compounds of picramide with *aromatic bases* separate in crystalline form when warm concentrated alcoholic solutions of the bases are added to excess of picramide; they give off the base at 100° . The *aniline-compound*, $C^6H^2(NO^2)^3NH^2.C^6H^7N$, forms black shining needles or prisms; the *paratoluidine* and *dimethylaniline-compounds* also form black shining crystals (Mertens, *Ber.* xi. 843). Hepp (*Bull. Soc. Chim.* [2], xxx. 4) also describes compounds of picramide with aniline, which differ from those obtained by Mertens, in giving off the whole of the aniline on exposure to the

PICRIC ACID, $C^6H^2(NO^2)_3OH$. Syn. with Trinitrophenol. See PHENOL (p. 1528).

PICRO-ALUNOGEN. A magnesio-aluminic sulphate occurring in stalactites in the iron-mine of Vignoria, Elba. An analysis by G. Roster (*Jahrb. f. Min.* 1877, 531) gave:

SO ³	Al ² O ³	MgO	K ² O	CoO	H ² O
36.387	9.160	8.189	0.368	trace	45.690 = 99.794

agreeing nearly with the formula $2MgSO^4, Al^2S^3O^{12} + 28H^2O$, which requires 36.80 per cent. SO³, 9.48 Al²O³, 7.36 MgO, and 46.36H²O, and showing that the mineral is nearly allied to pickeringite, $MgSO^4, Al^2S^3O^{12} + 22H^2O$ (v. 583).

PICROPHARMACOLITE. A native calcium arsenate allied to pharmacolite (p. 1513).

PICROROCCELLIN. A bitter substance obtained from *Rocella fuciformis* (q.v.)

PICROSCLEROTINE. A bitter and highly poisonous alkaloid obtained from ergot of rye (Dragendorff, *Russ. Zeitschr. Pharm.* xvi. 609; *Chem. Centr.* 1878, 125, 141; *Chem. Soc. J.* xxxiv. 518; Blumberg, *Pharm. J. Trans.* [3], ix. 23, 66, 147; *Chem. Soc. J.* xxxvi. 270).

PICROTEPHROÏTE. A light red mineral from Laangban in Norway, which may be regarded as tephroïte (Mn^2SiO^4 , v. 254), in which the manganese has been partly replaced by magnesium. An analysis by Pajkull (*Jahresb. f. Min.* 1878, 209) gave:

SiO ²	MnO	CaO	MgO	Loss on ignition
33.70	51.19	0.95	12.17	0.44 = 98.45

PICROTOXIN (Paternò a. Ogialoro, *Gazz. chim. ital.* 1876, 531; 1877, 193). The composition of this substance has hitherto been represented by the formula $C^{12}H^{14}O^3$, deduced by Barth from the analysis of a dibromo-derivative, $C^{12}H^{12}Br^2O^3$, and a mononitro-derivative, $C^{12}H^{13}(NO^2)O^3$, which he prepared and analysed, and from older analyses of the substance itself (iv. 643). Paternò a. Ogialoro, however, having prepared a specimen of picrotoxin, the purity of which was guaranteed by the fact of its melting point remaining constant at 199°–200°, even after repeated fractional crystallisation, found that it gave, as the mean of five closely agreeing analyses, 59.27 p.c. C. and 5.52 H., whence they deduce the formula $C^{12}H^{10}O^4$, which requires 59.34 per cent. C. and 5.49 H., whereas $C^{12}H^{14}O^3$ requires 60.50 C. and 5.88 H. By the action of bromine on picrotoxin, a crystalline mass was obtained containing only 21.39 per cent. bromine, whereas Barth's formula of the dibromo-compound requires 40 per cent. The hot alcoholic solution of this brominated compound deposited, on cooling, crystals which were free from bromine, sparingly soluble in alcohol, became coloured at 240°, and decomposed completely at 253°, and therefore did not consist of picrotoxin.

By saturating an ethereal solution of picrotoxin with hydrochloric acid, Paternò a. Ogialoro obtained a crystalline compound, $C^{22}H^{20}O^{11} = 3C^6H^{10}O^4 - H^2O$, insoluble in all ordinary solvents, and melting at a temperature above 310°. This compound, which they call *picrotoxide*, is also formed by the action of acetyl chloride and other dehydrating agents on picrotoxin. Subsequently, however, by the action of bromine on picrotoxin suspended in ether, they obtained a brominated compound, $C^{13}H^{13}BrO^6$, and a body having the composition $C^{13}H^{14}O^7$ or $C^{13}H^{16}O^6 + H^2O$. This substance they regard as a *hydrate of picrotoxide*, assigning to picrotoxide the formula $C^{13}H^{16}O^6$, which gives nearly the same percentage composition (61.65 C., 5.48 H., and 32.87 O.) as the formula $C^{22}H^{20}O^{11}$ (61.36 C., 5.31 H., and 33.33 O.) A *diacetyl-derivative*, $C^{15}H^{16}(C^2H^3O)^2O^7$, is formed by the action of acetyl chloride on the hydrate of picrotoxide. The whole subject seems to require further investigation.

PICRYLAMINES and **PICRYL-NITRANILINES**. Bases produced by the action of picryl chloride on the nitranilines. See BENZENE, NITRAMIDO- (p. 199).

PIGMENTS. On the black pigment of Hair and Feathers, see FEATHERS (p. 461).

A *green* pigment, prepared by decomposing barium chromate with sulphuric acid, and heating the chromium trioxide thereby liberated to bright redness, is described by T. Douglas (*Chem. News*, xl. 59; *Chem. Soc. J.* xxxvi. 987).

A fine *white* pigment, possessing great covering power when mixed with oil, is obtained by precipitating zinc chloride or sulphate with an alkaline sulphide, calcining the dried precipitate in a furnace, and levigating it by raking it out, while quite hot, into vats of cold water (Phipson, *Chem. News*, xxxviii. 105; *Chem. Soc. J.* xxxiv. 1017).

PILINITE. A mineral, hitherto regarded as a zeolite, occurring in felted needles, together with quartz, epidote, and desmin, in cavities of the granite of Strigau in Silesia. From microscopic measurements it is inferred to belong to the orthorhombic system, and in the flexibility of the needles it resembles the silicates of the asbestos-group. Sp. gr. 2.263 at 15°. Analysis gave:

SiO ²	Al ² O ³ , Fe ² O ³	CaO	Li ² O	H ² O
55.70	18.64	19.51	1.18 *	4.97 = 100

with traces of magnesia, soda, and potash. These numbers may be represented by the formula $\text{Ca}^2\text{Al}^2\text{Si}^4\text{O}^{15} + n\text{q} = 2\text{CaO}, \text{Al}^2\text{O}^3, 5\text{SiO}^2, \text{H}^2\text{O}$ (A. v. Lasaulx, *Jahrb. f. Min.* 1876, 358).

PILOCARPENE and PILOCARPINE. See JABORANDI (p. 1141).

PIMARIC ACID, $\text{C}^{20}\text{H}^{30}\text{O}^2$. This acid resin, which Laurent obtained from galipot, the hardened turpentine of *Pinus maritima* (iv. 645), has been further examined by A. Caillot (*Bull. Soc. Chim.* [2], xxi. 387). When fresh galipot, after washing with cold alcohol, is dissolved in twice its weight of 85 per cent. alcohol at 60°, and the solution is quickly cooled, pimaric acid separates in small crystals exhibiting the characters described by Laurent, including the melting point, 125°. Under the microscope, these crystals present the appearance of elliptic laminae, gradually changing into octagons. The alcoholic solution is strongly laevogyrate, and the more so as it is more dilute. The rotation of a 5.8 p. c. solution for the line D is -92.7; that of a 24.8 p. c. solution, -78.6.

The properties of pimaric acid are not altered by repeated crystallisation from a rapidly cooled solution in warm alcohol; but if it be dissolved to saturation in boiling alcohol and the solution left to cool very slowly, it separates in hard crusts which redissolve but slowly. At each repetition of this treatment, the melting point of the acid rises, and its rotatory power becomes less. When an alcoholic solution of the acid is heated in a sealed tube, it gradually loses the whole of its laevorotatory power, and ultimately becomes dextrorotatory. The acid thus altered by boiling with alcohol consists of three portions, viz.: (1). *Dextropimaric acid* (rotatory power + 56°), slightly soluble in cold alcohol, crystallising in rectangular plates, and melting at a temperature above 200°. (2). Laurent's *pyromaric acid* having a laevorotatory power of -66°, more soluble than the preceding, melting at 145°, and separating from warm alcohol in hemi-ellipses, which change into triangular laminae, and sometimes into crystals resembling galena. (3). A feebly laevorotatory acid, which hitherto has not been completely separated from the accompanying residues of the other two. The same alteration, though less complete, is produced in pimaric acid by simple dissolution in ethyl acetate, chloroform, benzene, turpentine-oil, and especially in carbon bisulphide. The acid contained in the latter solution had a rotatory power of only -11.5, which is increased to -37 on expelling the carbon sulphide and dissolving the residue in alcohol. A hot solution of pimaric acid in aqueous sodium carbonate yields crystals, not of sodium pimarate, as stated by Duvernoy, but of dextropimarate and pyromarate, while the sodium salt of the third acid above mentioned remains in solution (Caillot).

The sodium or calcium salt of pimaric acid yields by dry distillation propylene, amylene, propione, and a terebene (Bruylants, *Instit.* 1876, 238).

PIMELIC ACID, $\text{C}^7\text{H}^{12}\text{O}^4 = \text{C}^7\text{H}^{10}(\text{COOH})^2$. An acid having this composition was found by Laurent among the products of the oxidation of oleic acid by nitric acid; and similar products were obtained by Bromeis, Gerhardt, Sacc, and Arppe, by the action of nitric acid on wax, spermaceti, and other fatty bodies (iv. 646). All these, however, appear to have been impure products, and, according to Arppe, were for the most part nothing but mixtures of adipic and succinic acids (*Jahresb. f. Chem.* 1864, 377). Two definite modifications of the acid $\text{C}^7\text{H}^{12}\text{O}^4$ are, however, known, one called *pimelic acid*, obtained by the action of melting potash on camphoric acid (Hlasiwetz a. Grubowski, vi. 389), and by saponification of amylene dicyanide, $\text{C}^3\text{H}^{10}(\text{CN})^2$ (Bauer a. Schuler, *Ber.* x. 2031); the other, called *α -pimelic acid*, by the action of nitric acid on suberone (Dale a. Schorlemmer, *Chem. Soc. J.* xxvii. 935), and by the reducing action of hydriodic acid and red phosphorus on furonic acid (Baeyer, p. 834).

Pimelic acid.—To obtain this acid by saponification of amylene dicyanide, the preparation of which in the pure state appears to be difficult, Bauer a. Schuler allow an alcoholic solution of potash to flow in a slow stream into a heated mixture of amylene dibromide and potassium cyanide; distil off the alcohol, together with monobromamylene, after the heat has been continued for some time; mix the residue with sulphuric acid; and extract the pimelic acid, thus set free, with ether. The calcium

* Determined by difference.

salt of the acid thus obtained exhibited the characteristic properties of that of the pimelic acid prepared by Kachler from camphoric acid. The process above described yielded also, together with a small quantity of formic acid, another acid isomeric with pimelic acid, which, however, was not obtained pure (Bauer a. Schuler).

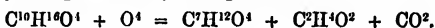
Pimelic acid prepared from camphoric acid is usually obtained, after purification, in transparent crystalline crusts, sometimes, however, in distinct crystals which, according to measurements by v. Zepharovich (*Wien. Akad. Ber.* lxxiii. [1 Abth.] 7) of crystals prepared by Wreden (*Liebig's Annalen*, clxiii. 323), belong to the triclinic system. $a : b : c = 0.4971 : 1 : 0.5992$. In the first octant (upper, front, right), $\alpha = 81^\circ 50'$; $\beta = 100^\circ 2'$; $\gamma = 85^\circ 6'$. Observed forms $\infty \bar{P} \infty$, $\infty \bar{P} \infty$, $0P$, $\bar{P}' \infty$, $\bar{P} \infty$, $2\bar{P} \infty$, $\bar{P} \infty$. Angle $0P : \infty \bar{P} \infty = 99^\circ 12'$; $0P : \infty \bar{P} \infty = 79^\circ 7'$; $\infty \bar{P} \infty : \infty \bar{P} \infty = 96^\circ 29'$; $0P : \bar{P}' \infty = 32^\circ 51'$. Cleavage perfect parallel to $\infty \bar{P} \infty$ and $\bar{P} \infty$. The trace of the plane of the optic axes forms on $\infty \bar{P} \infty$ with the obtuse edge $a c$ an angle of $59^\circ 5'$. Angle of optic axes in oil = 70° ; the first (positive) median line falls in the right upper octant.

Pimelic acid melts at 114° , is very soluble in water, alcohol, or ether, and has a taste like that of tartaric acid. The ammonium salt forms very soluble, hygroscopic leaflets containing $C^7H^{10}(NH_4)^2O^4$. The sodium salt is very soluble, and contains $C^7H^{10}Na^2O^4$. The barium salt is exceedingly soluble, and its solution evaporated under the air-pump first deposits plates and then dries up to a porous mass, which, when dried at 200° , contains $C^7H^{10}BaO^4$. The magnesium salt dries up to an amorphous mass, containing $C^7H^{10}MgO^4$. The copper salt was obtained as a green precipitate, which, when dried at 160° , contained $C^7H^{10}CuO^4$. A solution of the ammonium salt is not precipitated by the salts of manganese, ferrous, zinc, cobalt, nickel, chromium, cadmium, or mercurous, but it is precipitated by the salts of ferric, aluminium, lead, or bismuth. The ethylic ether, $C^7H^{10}(C^2H_5)^2O^4$, prepared by passing hydrochloric acid into an alcoholic solution of pimelic acid, is a heavy oil having a fruity odour, and boiling at 236° – 240° .

Pimelic anhydride, $C^7H^{10}O^3$, produced by distillation of the acid, is a colourless liquid boiling at 245° – 250° , and reconverted into the acid by hot dilute alkalis.

Pimelic chloride, $C^7H^{10}Cl^2O^2$, obtained by treating the acid with phosphoric chloride and heating the product at 120° , distils, with partial decomposition, at 210° .

When pimelic acid is treated either with bromine or with bromine and water, amorphous products are obtained, and in the former case butyric acid is also formed. This acid is likewise produced when pimelic acid is fused with potash: hence it is highly probable that the higher fatty acids which accompany pimelic acid in its production from camphoric acid result from the decomposition of butyric acid. Assuming this, the reaction which takes place in the preparation of pimelic acid from camphoric acid, $C^{10}H^{16}O^4$, may be represented by the equation:

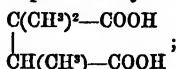


(Kachler, *Liebig's Annalen*, clxix. 168).

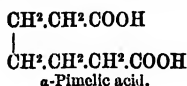
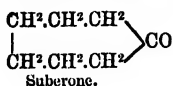
α -Pimelic acid is produced: 1. By oxidation of suberone with nitric acid, $C^7H^{12}O + O^2 = C^7H^{12}O^4$. 2. By heating furonic acid with 5 pts. of hydriodic acid (b. p. 127°) and $\frac{1}{2}$ pt. red phosphorus at 200° : $C^7H^{10}O^3 + 3H^2 = C^7H^{12}O^4 + H^2O$ (Baeyer, *Ber.* x. 1368).

α -Pimelic acid is distinguished from pimelic acid by its melting point, 103° (D. a. S.), 100° (Baeyer); its crystalline form, which is very much like that of meconic acid (p. 1269); and the property exhibited by its calcium salt, $C^7H^{10}CaO^4$, of dissolving in cold more freely than in hot water. The barium salt, $C^7H^{10}BaO^4 + H^2O$, forms transparent, tabular, very soluble crystals; the silver salt, $C^7H^{10}Ag^2O^4$, is a heavy, white precipitate, not altered by light, slightly soluble in boiling water (Dale a. Schorlemmer).

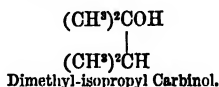
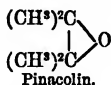
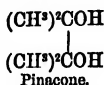
Constitution of the isomeric Pimelic acids.—Both these acids are amylenedicarboxylic acids. Supposing, then, that the amylenecyanide from which Bauer a. Schuler obtained pimelic acid contained ordinary amylenes, i.e. trimethyl-ethylene (p. 80), it follows that pimelic acid must be represented by the formula



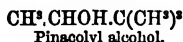
and if suberic acid be regarded as a normal compound, its ketone (suberone), and the α -pimelic acid formed therefrom will be represented by the following formulæ:



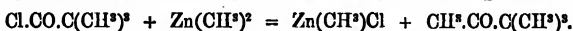
PINACOLIN, $C^6H^{12}O$. This compound, which Fittig obtained by dehydration of pinacone, or hexylene-glycol, $C^6H^{14}O^2$ (iv. 617), is regarded by Friedel a. Silva (*Compt. rend.* lxxvi. 226) as an anhydride of pinacone; and pinacolyl-alcohol, $C^6H^{14}O$, produced by the action of sodium or sodium-amalgam on pinacolin (vii. 982), is regarded by the same chemists as a tertiary hexyl-alcohol, viz. *dimethyl-isopropyl-carbinol*, the relations between the three bodies being represented by the following formulæ:



But the true dimethyl-isopropyl carbinol produced by treating isobutyryl chloride with zinc-methyl, and decomposing the product with water (p. 1035), differs considerably in physical properties from pinacolyl alcohol, and the formation of the latter by hydrogenation of pinacolin, and its reconversion into that body by oxidation, show that it is a secondary alcohol, viz., *methyl-katabutyl carbinol*, of which pinacolin is the ketone:



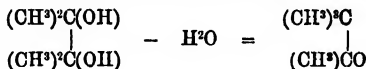
This view of the constitution of pinacolin is confirmed by its formation from trimethyl-acetyl chloride and zinc-methyl, as observed by Butlerow (p. 1148):



A further confirmation of the same view is afforded by the formation of trimethyl-acetic (pivalic) acid (p. 1501), by oxidation of pinacolin, observed by Friedel a. Silva:



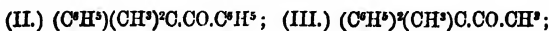
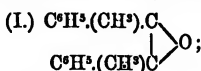
The formation of pinacolin from pinacone (tetramethyl-glycol) may be represented by the equation



(Butlerow, *Ber.* vi. 1254).

On the homologues of pinacolin obtained by the action of trimethyl-acetyl chloride on zinc-ethyl, and of ethyl-dimethyl-acetyl chloride on zinc-methyl and zinc-ethyl respectively, see KETONES (p. 1148).

Phenyl-methyl Pinacolins.—Phenyl-methyl ketone (acetophenone) might be expected to yield three pinacolins, represented by the following formulæ:



but, although several products are formed by the long-continued action of zinc and strong hydrochloric acid on an alcoholic solution of acetophenone, only one of the resulting pinacolins has been isolated viz., no. III: The oily liquid boiling between 300° and 330° , which remains after distilling the crude product in a current of steam, to remove unaltered acetophenone, deposits crystals of this acetophenonepinacolin; and the mother-liquor yields, on fractional distillation, pinacolin, acetophenonepinacone, a substance of unknown composition, melting at 107° , and an oil boiling below 300° , which does not solidify, and may perhaps contain small quantities of the pinacolins I. and II. *Pinacolin* III. crystallises in rhombic prisms, which are soluble in benzene, chloroform, ether, glacial acetic acid, and hot alcohol. It melts at 41° , boils at 310° , and is decomposed by soda-lime into acetic acid and diphenylmethylmethane, $(C^6H^5)^2CH.CH^3$. This hydrocarbon boils at 264° , yields benzophenone on oxidation, and is identical in its properties with the hydrocarbon described by Goldschmiedt and by Radziszewski as diphenylethane (p. 673). By the action of hydriodic acid and red phosphorus, the pinacolin is reduced to diphenylethylmethylmethane, $(C^6H^5)^2C(CH^3)(C^6H^5)$, which crystallises in transparent plates or prisms melting at 127.5° , and is perhaps identical with the diphenyldimethylethane obtained by Engler a. Bethge from phenylmethyl-carbinyl bromide (p. 668) and by Radziszewski (*Ber.* vii. 142) by the action of zinc-dust on a mixture of ethyl-benzene and bromethylbenzene (Thörner a. Zincke, *Ber.* xi. 1988).

On *Benzpinacolins* and *Tolyl-phenyl Pinacolins*, $C^{10}H^{20}O$, see KETONES (p. 1155).

PINACOLYL ALCOHOL, $C^6H^{10}O = CH^2 \cdot CHOH \cdot C(CH^3)^2$. See HEXYL ALCOHOLS (p. 1035).

PINACONES. The six-carbon pinacone, $C^6H^{10}O^2$, is formed by treating tetramethylethylene bromide, $(CH^3)^2C=C(CH^3)^2$, with silver acetate, and saponifying the resulting tetramethyl-ethylene acetate with baryta. A crystalline hydrate of pinacone, $C^6H^{10}O^2 \cdot 6H^2O$, is thus obtained, melting at $46 \cdot 3^\circ$, and identical in every respect with that which is produced by the action of sodium-amalgam on aqueous acetone (iv. 648): hence it follows that pinacone is tetramethylethylene glycol, $(CH^3)^2(OH)C-C(OH)(CH^3)^2$ (Pawlow, *Liebigs Annalen*, cxvi. 122).

The following method of preparing pinacone in considerable quantity is given by Friedel a. Silva (*Bull. Soc. Chim.* [2], xix. 289). A solution of potassium carbonate (of such strength as not to dissolve any perceptible quantity of acetone, but to be easily decomposed by sodium) is introduced into a row of 14 to 16 flasks; 600–700 grams of acetone are distributed between the same vessels, and 200 to 250 grams of sodium, in pieces about the size of a pea, are thrown in. The sodium sinks in the layer of acetone, and comes in contact with the watery layer, where it liberates hydrogen, which is almost completely fixed by the acetone. After the whole of the sodium has been introduced, the upper layer of the liquid is fractionally distilled, and in this manner from 250 to 300 grams of pseudopropyl alcohol are obtained, together with 60 to 65 grams of anhydrous pinacone, which may be dissolved in water, and crystallises out as the pure hydrate.

Pinacolyl-pinacone, $C^{12}H^{20}O^2$, is formed in the preparation of pinacolyl alcohol from pinacolin (vii. 982), and remains, on distilling off the alcohol, in the form of a crystalline mass which melts at 69° (Friedel a. Silva).

Benzpinacone, $C^{16}H^{20}O^2$. This compound, which Linnemann obtained (iv. 648) by the action of zinc and dilute sulphuric acid on diphenyl ketone (benzone or benzophenone), is usually regarded as tetraphenyl glycol, $(C^6H^5)^2(HIO)C-C(OH)(C^6H^5)^2$, that is to say, as related to diphenyl-ketone in the same manner as ordinary pinacone to acetone. If this were its true composition, it might be expected to form secondary as well as primary ethers by substitution of alcohol-radicles for the hydrogen of the two hydroxyl-groups. Thörner a. Zincke, however (*Ber.* x. 1473), after repeated efforts, have found it impossible to effect this substitution, so that the constitution of the pinacone must for the present remain undecided.

Benzpinacone, heated for six to eight hours with hydriodic acid and red phosphorus, is converted into tetraphenylmethane, $C^6H^2(C^6H^5)^4$, which is easily separated from a small quantity of the unaltered pinacone by extraction with ether, and crystallises in large prisms melting at 206° (Graebe, *Ber.* viii. 1054).

According to Thörner a. Zincke, benzpinacone, when fused or distilled, is not converted into a physical isomeride, as stated by Linnemann, but is resolved into benzophenone and benzhydrol, $C^{20}H^{20}O^2 = C^{12}H^{10}O + C^8H^{10}O$, the decomposition being complete even at the melting point of the pinacone.

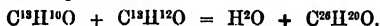
Benzpinacolins, $C^{20}H^{20}O$. Thörner a. Zincke (*Ber.* x. 1473; xi. 68, 1396). Two bodies of this composition, distinguished as α - and β -pinacolins, are produced by the action of acids and acid chlorides on benzpinacone, also by heating diphenyl ketone in alcoholic solution with zinc and hydrochloric acid. At the same time there is formed a large quantity of benzpinacone, whence it would appear that pinacones are intermediate products of the conversion of ketones into pinacolins.

α -Benzpinacolin may be obtained pure by treating an alcoholic solution of diphenyl ketone with zinc and dilute sulphuric acid, and heating the product, which is a mixture of the pinacolin and pinacone, to 190° – 200° , whereby the pinacone is resolved into benzophenone and benzhydrol, which may be removed by ligroin, leaving the α -pinacolin to be further purified by crystallisation from alcohol. Thus prepared, it crystallises in tufts of needles which melt at 204° – $204 \cdot 5^\circ$; it dissolves sparingly in cold alcohol and glacial acetic acid, more easily when heated. Benzene, chloroform, &c., dissolve it easily; ether, however, only slightly. When α -benzpinacolin is heated with acetyl chloride, aqueous hydrochloric acid, or alcohol and sulphuric acid, it passes into the β -modification; oxidised by a solution of chromic anhydride in acetic acid, it is resolved into benzophenone and benzoic acid.

α -Benzpinacolin is identical with the tetraphenyl-ethylene oxide which Behr obtained by oxidation of tetraphenyl-ethylene (vii. 1150). This mode of formation, however, is not conclusive as to the constitution of the pinacolin, and does not determine whether it is an inner anhydride or an ether of benzophenone; neither are the products obtained on heating α -benzpinacolin with soda-lime more conclusive as to its constitution. The chief product is a hydrocarbon mixed with benzophenone and benzoic acid. This hydrocarbon has the empirical formula $C^{12}H^{10}$, and crystallises

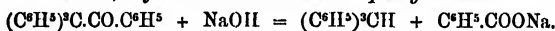
from hot alcohol or glacial acetic acid in well-formed colourless crystals, which melt at 243° – 244° , and at the same time turn yellow. Benzene, toluene, carbon bisulphide, and chloroform dissolve it easily, whilst it is less easily soluble in ether, ligroin, cold alcohol, or glacial acetic acid. Its solutions show a beautiful blue fluorescence, which is destroyed by picric acid. The properties of this hydrocarbon show plainly that it is not identical with tetraphenyl-ethylene, of which however it may be a polymeride. The determination of its molecular formula would throw great light on the constitution of α -benzpinacolin.

The resolution of benzpinacone into benzophenone and benzhydrol, which takes place in the preparation of the α -pinacolin, is accompanied by formation of water and of a body isomeric with the pinacolin:



This body forms beautiful colourless crystals, melts at 107° – 108° , and is identical with that which Linnemann obtained by the action of heat on benzhydrol. Linnemann represented it by the formula $(\text{C}^6\text{H}^5)^2\text{CH.O.CH}(\text{C}^6\text{H}^5)^2$, regarding it as ether of benzhydrol. Thörner a. Zincke, however, observe that it is formed by the action of heat on benzpinacone more easily than benzhydrol, which is in the first instance resolved into diphenylmethane and benzophenone: $2\text{C}^{13}\text{H}^{12}\text{O} = \text{C}^{13}\text{H}^{12} + \text{C}^{13}\text{H}^{10}\text{O} + \text{H}_2\text{O}$. Hence it appears most probable that this body is not an ether of benzhydrol, but that it is more nearly related to the α -pinacolin.

β -Benzpinacolin, $(\text{C}^6\text{H}^5)^2\text{C.CO.C}^6\text{H}^5$, melts at 178° – 179° . It yields by oxidation benzoic acid and triphenylcarbinol, $(\text{C}^6\text{H}^5)^3\text{C.OH}$, but no triphenylacetic acid, and therefore differs in its behaviour from the pinacolins of the fatty series. When heated to 300° with soda-lime, it yields benzoic acid and triphenylmethane:



By reduction with hydriodic acid and phosphorus, it yields a hydrocarbon, $\text{C}^{25}\text{H}^{20}$, presumably tetraphenylethane or triphenylbenzylmethane, $(\text{C}^6\text{H}^5)^3\text{C-CH}_2\text{-C}^6\text{H}_5$. This hydrocarbon is soluble in benzene, chloroform, carbon bisulphide, hot alcohol, and acetic acid, sparingly in ether, and crystallises from benzene in brilliant rhombic tables, which speedily turn opaque and fall to powder in the air. It crystallises from alcohol in beautiful long white prisms, which melt at 205° – 206° , and sublime in small needles at a higher temperature (Thörner a. Zincke).

Tolylphenyl pinacone, $\text{C}^{28}\text{H}^{26}\text{O}^2$, is formed from tolylphenyl ketone (p. 1154) in the same manner as benzpinacone from diphenyl ketone; it exhibits the same relations to solvents as the latter, but frequently does not separate from the alcoholic solution till after great concentration, and then crystallises in indistinct microscopic needles melting at 164° – 165° . Like benzpinacone, it is resolved by heating and by the action of alcoholic potash into tolylphenyl ketone and tolylphenyl hydrol, the latter of which has been obtained only in the liquid state: $\text{C}^{28}\text{H}^{26}\text{O}^2 = \text{C}^{14}\text{H}^{12}\text{O} + \text{C}^{14}\text{H}^{14}\text{O}$. By oxidation the pinacone is converted into tolylphenyl ketone.

Tolylphenyl pinacone, like benzpinacone, is converted by all etherifying agents—including zinc-chloride—into tolylphenyl pinacolins, and for the most part into the β -modification, which is the more stable of the two. The α -pinacolin is most easily obtained by mixing the alcoholic solution of the pinacone with a small quantity of hydrochloric acid, and leaving the mixture to itself for a while at ordinary temperatures (Thörner a. Zincke, *Ber.* x. 1474). See further, p. 1155.

PINE. Experiments by Fliche a. Grandeau (*Ann. Chim. Phys.* [4], xxix. 383; *Chem. Soc. J.* xxvii. 382) on the growth of the cluster pine (*Pinus Pinaster*) on different soils, show that this tree does not flourish on calcareous soils containing but a small proportion of potash. The ash of a twig of the plant with bark and leaves grown on such soil was found to be very poor in potash.

Experiments by the same chemists (*Ann. Chim. Phys.* [5], xi. 224) on the leaves of *Pinus laricio austriaca* yielded the following results: (1). From the opening of the bud to the fall of the leaf, the leaves of coniferous plants become continually richer in dry substance. (2). During the same time they lose part of their nitrogen, which is reabsorbed, while the proportion of ash increases. (3). The proportion of phosphoric acid, sulphuric acid, and potash in the ash diminishes. (4). The proportion of lime, iron, and silica increases. (5). For the proportion of magnesia and soda, no rule can be laid down. (6). Assimilation in coniferous leaves is very rapid in the first year, slackens at the beginning of the second, and afterwards ceases almost entirely. (7). The composition of the soil has a decided influence on the quality and quantity of coniferous leaves, this influence being, however, comparatively less when external conditions are favourable to growth. (8). Coniferous leaves have approximately the same composition as those of leafy trees, but they are always somewhat richer

in total amount of dry substance, poorer in nitrogen, and considerably poorer in ash, which, moreover, differs in composition from that of leafy trees. The removal of fallen leaves is injurious to the growth of coniferous forests. (9). For forest cultivation on poor soils, conifers are to be preferred to other trees; and for planting on a calcareous soil in a climate where only conifers will grow, *Pinus austriaca* is the best of all.

PINEY TALLOW. This tallow, obtained by boiling the fruits of *Vateria indica* (from Malabar) with water, forms a yellow-green mass having a density of 0.91, melting at 30°, and consisting of a mixture of 75 per cent. palmitic acid and 25 per cent. oleic acid. It may be bleached by boiling with a solution of nitre mixed with sulphuric acid, or by exposure to air and light. Candles made of it burn better than common tallow candles, and do not give off any odour when blown out (G. Dal-Sie, *Gazz. chim. ital.* viii. 107).

PINK. The ash of the garden pink, *Dianthus Caryophyllus*, has been analysed by R. Andreasch (*J. pr. Chem.* [2], xviii. 204) with the following results:

	Roots	Stalks	Leaves	Flowers
K ² O	23.33	23.00	35.51	49.41
Na ² O	0.85	—	—	—
CaO	45.26	45.16	27.69	5.85
MgO	4.43	5.48	8.27	3.68
Fe ² O ³	3.83	7.95	6.42	7.19
Mn ² O ⁴	—	—	—	traces
Al ² O ³	2.56	traces	—	—
P ² O ⁵	11.22	10.25	10.94	14.84
SO ²	2.59	6.46	4.59	4.04
SiO ²	5.34	0.61	3.71	4.25
NaCl	0.59	0.44	0.71	2.35
KCl	—	0.65	2.16	8.39
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
Percentage of ash . . .	5.04	5.26	4.44	5.59

PIROLITE. See MAGNESITE (p. 1244: further *Min. Mitth.* 1874, 281; *Jahresb. f. Chem.* 1874, 1314).

PIPERIC ACID, C¹²H¹⁰O⁴. The constitution of this acid has been studied by Fittig a. Mielk (*Liebig's Annalen*, clxxii. 134). Piperonylic acid, C¹²H¹⁰O⁴, the product of oxidation of piperic acid, having been shown by former experiments (vii. 983) to have the constitution represented by the formula $\text{CH}^2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}^6\text{H}^3 \cdot \text{COOH}$, it appeared

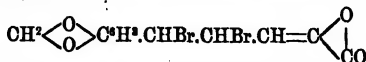
probable that piperic acid might be represented by $\text{CH}^2 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}^6\text{H}^3 \cdot \text{C}^3\text{H}^5\text{O}^2$, the group C³H⁵O² being the residue of an acid belonging to the sorbic acid series, and resolvable into —CH=CH—CH=CH—COOH; and these suppositions have been verified by the more exact investigation of the products obtained by the action of bromine on piperic and hydropiperic acids.

Action of Bromine on Piperic acid.—When 1 mol. finely divided piperic acid is suspended in anhydrous carbon sulphide cooled by ice, and 2 mols. bromine are gradually added, a crystallogranular powder is formed, consisting of the *tetrabromide of piperic acid*, or *tetrabrompiperhydronic acid*, C¹²H¹⁰O⁴Br⁴, or



This acid, when heated to 160°–165°, decomposes with somewhat violent evolution of gas, and melts to a brown viscid liquid. It dissolves readily in cold ether or alcohol, but cannot be recrystallised from the resulting solutions, as it is at the same time partly converted into an amorphous viscid mass, probably an ether or a decomposition-product of the tetrabrominated acid. On treating this acid with cold dilute soda-ley, or boiling it with sodium carbonate, the whole of the bromine is removed as sodium bromide, and piperonal, C⁸H⁶O², is formed, which may be obtained in considerable quantity by warming or agitating the product with ether. When, on the other hand, the tetrabromo-compound is boiled with water, it is converted into an oil which solidifies on cooling, and on repeated crystallisation from dilute alcohol, yields colourless shining prisms slightly soluble in cold alcohol and melting at 136°. This compound, which Fittig a. Mielk formerly obtained by the successive action of bromine and

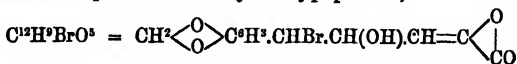
sodium carbonate (vi. 946), is likewise produced by treating the tetrabrominated acid with a cold solution of sodium carbonate. Its composition is represented by the formula $C^{12}H^8Br^2O^4$, which might be that of a dibromopiperic acid. Nevertheless, the compound in question is not an acid, since it is quite insoluble in aqueous sodium carbonate, and is not immediately altered by potash-ley, even when somewhat concentrated. It is rather to be regarded as an anhydride analogous to lactide, and represented by the formula :



or



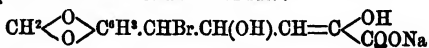
and may be designated as dibromopiperide. When heated with soda-ley or boiled for some time with sodium carbonate, it is completely resolved into piperonal and hydrobromic acid, but when subjected to the regulated action of sodium carbonate, it yields an intermediate product, bromhydroxypiperide,



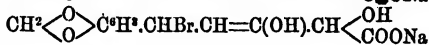
or



which, after filtration from a small quantity of the unaltered dibromo-compound, and removal, by agitation with ether, of the piperonal—which is always formed at the same time by complete decomposition of another portion of the latter—remains dissolved in the alkaline liquid. This liquid, when acidulated, deposits at first a small quantity of a brown amorphous precipitate which must be quickly separated by filtration, and the filtrate gradually deposits the bromhydroxypiperide in small crystals; it may also be dissolved out of the alkaline solution by agitation with ether. It is contained in the alkaline liquid in the form of a sodium salt:



or



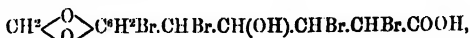
the acid of which, however, when set free by sulphuric acid, immediately changes into the corresponding anhydride, viz. bromhydroxypiperide. This compound is but sparingly soluble in hot and nearly insoluble in cold water, very easily soluble in hot alcohol, less easily in cold alcohol and in ether, requiring 100 pts. of the latter at 10° to dissolve it. The crystals, according to measurements by Reusch, belong to the monoclinic system, and exhibit the combination $\infty P. \infty P \infty. 0P. 2 \infty. -\frac{1}{2}P$, with tabular development in the direction of the clinopinacoid. Axial ratio $a : b : c = 0.8005 : 1 : 1.1954$. Angle $ac = 119^\circ 16'$. The plane of the optic axes coincides with the plane of symmetry. In its chemical relations, bromhydroxypiperide agrees almost exactly with dibromopiperide; it has no acid properties, but is gradually decomposed by alkalis, with reddening and formation of piperonal.

When piperic acid is treated with an ethereal solution of bromine, and the product is shaken up with aqueous sodium carbonate, small colourless nacreous laminae separate, which were formerly supposed to have the composition $C^6H^8Br^2O^6$ (vi. 936), but have been shown by later experiments to consist of the sodium salt, $C^{12}H^8Br^2NaO^5 + 1\frac{1}{2}H^2O$, of an acid, $C^{12}H^{10}Br^2O^5$, which may be regarded as a derivative of the saturated compound, $C^{12}H^{14}O^5$ (piperhydronic acid), and named *tetrabromhydroxypiperhydronic acid*. This acid, separated from the solution of the sodium salt by hydrochloric acid, is almost insoluble in water, crystallises from dilute alcohol in small transparent crystals, begins to decompose at a temperature above 100° , and melts with violent decomposition at 155° . When drenched with aqueous sodium carbonate, it is instantly converted into the sparingly soluble sodium salt, but turns yellow after prolonged contact, and decomposes on boiling, with formation of monobromopiperonal. The calcium salt, $(C^{12}H^8Br^2O^5)^2Ca + 2H^2O$, separates on adding calcium chloride to a dilute solution of the sodium salt, in small white shining sparingly soluble laminae. The barium salt, $(C^{12}H^8Br^2O^5)^2Ba + 3H^2O$, resembles the sodium salt, but is still less soluble. Both these salts become anhydrous at 90° .

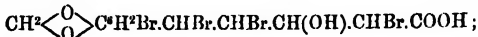
By subjecting tetrabromhydroxypiperonic acid to the regulated action of sodium carbonate (as in the preparation of bromhydroxypiperide from dibromopiperide, p. 1631), it is possible to obtain a compound intermediate between that acid and its

ultimate product of decomposition, monobromopiperonal. This compound, *dibromhydroxypiperide*, $C^{12}H^8Br^2O^3$, separates from the ethereal solution on spontaneous evaporation, in large well-defined prisms; it is but slightly soluble in water, more soluble in alcohol and ether. It is not an acid, and is not attacked by solution of sodium carbonate at ordinary temperatures, but is converted thereby on heating into monobromopiperonal.

Tetrabromhydroxypiperhydronic acid may be derived from the tetrabromide of a bromopiperic acid, $CH^2\langle O \rangle C^6H^2Br.CHBr.CH(OH).CHBr.CHBr.COOH$, and its constitution may be represented either by the formula



or by



and that of dibromhydroxypiperide by either of the corresponding formulæ



or



Monobromopiperonal, heated with potassium permanganate, is converted into monobromopiperonylic acid, $C^6H^3BrO^4$, which crystallises well, melts at 204° – 205° , and sublimes without decomposition.

Action of Bromine on Hydripiperic acid, $C^{12}H^{12}O^4$.—This acid, treated with bromine in the manner described for the preparation of tetrabromopiperhydronic acid from piperic acid (p. 1631), is converted into dibromopiperhydronic acid, $C^{12}H^{12}Br^2O^4$, which is insoluble in water, sparingly soluble in carbon sulphide, easily in ether, and separates therefrom in small colourless crystals, melting at 135° – 136° . It decomposes at about 150° , and suffers partial decomposition on solution in warm alcohol; dissolves easily and without decomposition in cold aqueous sodium carbonate, but is decomposed on boiling therewith, without, however, yielding piperonal. When heated with caustic soda-solution, it does not yield either piperonal or any other volatile body, but the solution when evaporated deposits sodium piperate. From this reaction of the dibrominated acid—which is analogous to that of the corresponding brominated acids of the acrylic series—it follows that hydripiperic acid has the constitution represented by the formula $CH^2\langle O \rangle C^6H^3.CH^2.CH^2.CH=CH.COOH$, the second possible formula being excluded by the non-production of piperonal by the action of alkalis on this acid—which is inconsistent with the attachment of bromine to the CH-group directly connected with the benzene-nucleus. This formula is, moreover, in accordance with the action of melting potash on hydripiperic acid, whereby proto-catechuic and acetic acids are produced, but no butyric acid. In this reaction, a dihydroxyphenylpropionic acid, $C^6H^2(OH)^2.CH^2.CH^2.COOH$, is perhaps first formed, and afterwards resolved, like similar acids under the influence of potash, into the two acids above mentioned.

PIPERIDINE, $C^8H^{11}N$. This base is formed, together with pyrethric acid, by the action of alcoholic potash on pyrethrin, a crystalline substance obtained from *Radix Pyrethri* (R. Buchheim, *N. Rep. Pharm.* xxv. 335).

Piperidine is not decomposed by fuming hydrochloric acid at 300° . Its hydrochloride combines directly with bromine to form a crystalline addition-product, which rapidly decomposes even at the ordinary temperature. On heating this bromine-compound, or a mixture of bromine and piperidine hydrochloride, in sealed tubes at 200° , hydrobromic acid and a small quantity of bromoform are produced, and on the addition of water to the contents of the tubes, a substance having the composition $C^8H^8Br^2NO$ separates out in crystalline plates. The crystals are almost insoluble in cold water and ether; they dissolve in ammonia or soda-solution, but are reprecipitated by dilute acids. They are decomposed by heat without melting. When platinum chloride is added to a solution of this substance in strong hydrochloric acid, the *platinochloride*, $2(C^8H^8Br^2NO.HCl)PtCl^4$, is deposited in long needles, which are decomposed by water. The *silver salt*, $C^8H^8AgBr^2NO$, is a sparingly soluble crystalline powder; the *methyl ether*, $C^8H^9(CH^3)Br^2NO$, crystallises in white needles, which melt at 192° .

The existence of these compounds seems to indicate the presence of a hydroxyl-
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group in the piperidine derivatives, *e.g.* $C^3H^2Br^2(OH)N$; $C^3H^2Br^2(OAg)N$ (A. W. Hofmann, *Ber.* xii. 984).

PIPERIDYL- α -ALANINE or **PIPERIDYL- α -PROPIONIC ACID**, $C^8H^{10}NO^2 = CH^2-CH=N-C^3H^5-COOH$, is prepared by digesting ethyl α -chloropropionate for twenty-four hours at 100° in a sealed tube with excess of anhydrous piperidine. The product, consisting of piperidyl- α -alanine and piperidine hydrochloride, is boiled with barium hydrate to remove the piperidine, the barium is precipitated by sulphuric acid, and this acid by lead hydrate. The filtrate, when evaporated, leaves piperidyl- α -alanine, which crystallises from water and alcohol in prisms, and is precipitated from its alcoholic solution by ether, as a white syrupy mass convertible by trituration into a granular powder. It is tasteless and scentless, has a neutral reaction, and forms crystallisable salts both with bases and with acids. It does not form a stable compound with platonic chloride, but on mixing its aqueous solution with auric chloride, evaporating, dissolving the residue in alcohol, and evaporating the solvent, after filtration from separated gold, an aurochloride is obtained in stellate groups of needles, very soluble in water, less soluble in ether, insoluble in chloroform. By the influence of light and heat, it is partially decomposed, with separation of gold (J. Brühl, *Ber.* ix. 34).

PIPERINE, $C^{17}H^{19}NO^3$. For the extraction of this alkaloid from pepper, and its estimation, the following method is recommended by L. Cazeneuve a. Caillot (*Bull. Soc. Chim.* [2], xxvii. 290). Ground pepper is treated with twice its weight of slaked lime and a sufficient quantity of water, the whole being heated to boiling for a quarter of an hour. The solution is then evaporated to dryness on the water-bath, and the powder exhausted with commercial ether, from which the piperine can be obtained nearly pure on evaporation in large crystals of a faint straw-yellow colour. To obtain it perfectly pure, it must be dissolved in alcohol and recrystallised. The crystals obtained from the ether are, however, quite pure enough for determining the amount of alkaloid in the pepper. For this purpose, it is best to operate on 10 grams of pepper, and dry the piperine obtained from the ether solution at 100° :

Sumatra pepper	gave 8.1 per cent piperine (mean)
Black Singapore do. . . .	7.15 " " "
White do. do. . . .	9.15 " " "
Penang do. do. . . .	5.24 " " "

The superior richness of the white Singapore pepper in piperine is due to the absence of the inactive pericarp.

On the estimation of Piperine, see also PLANT-BASES.

PIPERONAL. On the formation of this aldehyde from tetrabrompiperhydronic acid, see PIPERIC ACID (p. 1631).

The vapour-density of piperonal has been found by W. Knecht (*Ber.* x. 1274) to be 5.181, agreeing nearly with the formula $C^8H^6O^3$, which requires 5.20.

PIPERONYLIC ACID, $C^8H^6O^4 = CH^2-\langle \bigcirc \rangle-C^3H^5-COOH$. *Methylene-protocatechuic acid* (p. 291).—This acid is a constituent of Coto-bark (p. 573). To obtain it therefrom, the bark, previously extracted with ether, is digested with milk of lime; the alkaline solution is acidified with hydrochloric acid, and agitated with ether; and the residue obtained on evaporating the ethereal solution is dissolved in hot alcohol, which on cooling deposits the piperonylic acid, as a white crystalline powder, melting at 229° , and beginning to sublime at 210° . Piperonylic acid dissolves in cold concentrated sulphuric acid, forming a yellow solution, which rapidly turns brown, and finally black, no gas being evolved during the process. Water produces in the yellow solution a yellow, and in the black solution a black precipitate, the filtrate in each case containing protocatechuic acid.

Mielch a. Fittig, by oxidising piperonylic acid with nitric acid, obtained oxalic and carbonic acids; but when concentrated nitric acid is allowed to act on the acid for a few minutes only, a mixture of nitropiperonylic acid and methylene-mononitro-catechol is formed. When piperonylic acid is added in small quantities to fuming nitric acid cooled to 0° , carbon dioxide is given off, and methylenedinitrocatechol is produced. In each case the nitro-products are precipitated from the acid mixture by the addition of caustic soda.

Nitropiperonylic or *Methylene-nitroprotocatechuic acid*, $C^8H^5(NO^2)O^4$, crystallises in yellow scales (m. p. 172°), which dissolve easily in water, and on the addition of caustic soda or potash to the aqueous solution, a yellow coloration is produced which turns blood-red on boiling. With ferric chloride no change is produced. This acid is monobasic; it forms well-crystallised salts, which burn vigorously when ignited (Jobst a. Hesse, *Ber.* xi. 1031).

PITTACAL. See PYROGALLOL.

PIVALIC ACID, $\text{C}^3\text{H}^{10}\text{O}^2 = \text{C}(\text{CH}_3)_2\text{COOH}$. See KETTOIC ACIDS (p. 1501).

PLAGIOCLASE. *Triclinic felspar.* See FELSPAR (pp. 770-775). The granular plagioclase, occurring in the limestone strata of Gieppersdorf near Strehlen, in Silesia, has been described and analysed by E. Schumacher (*Jahrb. f. Min.* 1878, 814; *Chem. Soc. J.* xxxvi. 903).

PLANT-BASES. The following method for the estimation and separation of plant-bases or vegeto-alkaloids, differing in several points from the well-known Stas-Otto method (i. 125), is given by Dragendorff (*Pharm. J. Trans.* [3], vii. 24). 1. The substances under examination are exhausted with water, and a small quantity of sulphuric acid (instead of tartaric acid and alcohol); the resulting solution is partly neutralised with magnesia and evaporated; and the syrupy residue is treated with alcohol mixed with dilute sulphuric acid. The alcoholic filtrate is freed from alcohol by distillation, and the aqueous residue is filtered, with addition of water if necessary, and shaken up at 40° with petroleum-ether, which takes up *piperine*, to be recognised by its reaction with strong sulphuric acid (blood-red coloration disappearing on addition of water, iv. 658).

2. The remaining aqueous solution is nearly neutralised with magnesia or ammonia and agitated with benzene, which takes up *caffeine*, *delphinine*, *colchicine*, *cubaine*, *digitalin* [which is not an alkaloid], and traces of *veratrine*, *physostigmine*, and *berberine*. Among these bodies, caffeine may be recognised by its reaction with chlorine-water and ammonia (or hydrochloric acid and potassium chlorate), giving the colour of murexid; digitalin by the red colour of its solution in strong sulphuric acid, changing to yellow or greenish on dilution with water (ii. 329; vi. 546); veratrine by the yellow colour which it gives with sulphuric acid, changing to crimson and ultimately to violet (v. 996). Solutions of colchicine and berberine leave on evaporation yellow residues, the former dissolving in strong sulphuric acid with dark yellow. The latter with olive-green colour, disappearing on evaporation, and leaving the liquid colourless. Colchicine and berberine may also be distinguished by their reaction with iodine, colchicine yielding with tincture of iodine a kermes-brown precipitate (i. 1081), while an alcoholic solution of a berberine salt, mixed with a dilute solution of iodine in potassium iodide, avoiding excess of iodine, deposits green spangles of a polarising salt resembling sulphate of iodoquinine (vi. 340). Delphinine is coloured light brown by sulphuric acid. Physostigmine is not coloured by sulphuric acid but may be recognised by the contraction of the pupil which it produces.

3. The slightly acid liquid is then shaken up with amyl alcohol, which takes up *theobromine*, as well as traces of *narcotine*, *aconitine*, and *atropine* [theobromine may be recognised by its property of gradually dissolving in water with yellowish colour, changing to blue on addition of ammonia; also by dissolving without colour in strong sulphuric acid]; and the residual aqueous liquid is treated with chloroform, which takes up from it *papaverine* and *thebaine*, together with small quantities of *narcine*, *brucine*, *physostigmine*, *berberine*, *veratrine*, and *narcotine*. Papaverine is recognised by the blue-violet colour which it gives with strong sulphuric acid; thebaine by the red colour which it gives with the same reagent.

4. The liquid separated from the chloroform extracts, instead of being made alkaline with soda-ley to separate morphine (as in the Stas-Otto method), is treated for that purpose with ammonia, which is added to it under a layer of petroleum-ether at 40° , the vessel being shaken immediately after the liquid has become alkaline. The petroleum-ether then dissolves *strychnine*, *brucine*, *quinine*, *emetine*, *veratrine*, *conine*, *nicotine*, and *papaverine*. Nicotine and conine may be dissolved out by water, and from the aqueous solution, after neutralisation with sulphuric acid, nicotine is precipitated by potassio-cadmic iodide in small crystals, conine in the amorphous state; the other bases, freed from petroleum ether and dried, are treated with ether, which takes up quinine, emetine, papaverine, and veratrine. From this mixture, the veratrine may be separated by dissolving the whole in the smallest possible quantity of dilute sulphuric acid, and precipitating with sodium carbonate, whereby only quinine, emetine, and papaverine are reprecipitated. Strychnine and brucine may be separated by means of alcohol, in which strychnine is nearly insoluble. Emetine is recognised by its action on the organism, the other alkaloids by known reactions.

5. The alkaline aqueous solution is next treated at 40° - 50° with benzene, whereby *quinine*, *cinchonine*, *atropine*, *hyoscyamine*, *aconitine*, *physostigmine*, and *codeine* are removed. Cinchonine remains behind on evaporating the solution of these bodies to dryness, and exhausting the residue with ether; on evaporating the ethereal extract, dissolving the residue in very dilute sulphuric acid, and mixing the solution with a slight excess of ammonia, quinine and aconitine are precipitated, whilst atropine,

hyoscyamine, and codeine remain in solution. Aconitine and quinine are separated by dissolving them in a very small quantity of hydrochloric acid, and adding platonic chloride, which throws down the quinine; and from the remaining solution, after removal of the platinum by hydrogen sulphide, the aconitine may be dissolved out by chloroform. Atropine may be distinguished from hyoscyamine, which it resembles in its action on the pupil, by the odour which it emits when heated with potassium dichromate and sulphuric acid.

6. The bases which may still be present in the alkaline aqueous residue are *morphine*, *solanine*, *curarine*, and a small quantity of *narceine*, together with traces of *berberine*. From this mixture, morphine and solanine, together with a small quantity of narceine, may be separated by acidulating with sulphuric acid, heating to 50° – 60° , covering the surface of the liquid with a layer of amyl alcohol, then adding excess of ammonia and agitating. The morphine then crystallises out from the amyl-alcoholic solution, and the solanine gelatinises as the liquid cools. Curarine, with traces of berberine and the remainder of the narceine, is separated from the last aqueous liquid by evaporating to dryness with pounded glass, digesting with alcohol, and evaporating, this treatment being repeated if necessary. Curarine is characterised by being for the most part an amorphous mass, and by giving with sulphuric acid alone a fine blue colour (ii. 186), and with sulphuric acid and potassium dichromate a violet colour like that produced by strychnine (v. 440).

On the distinguishing reactions of Plant-bases, see also Selmi (p. 55 of this volume).

PLANT-COLOURS. The following observations by H. C. Sorby (*Proc. Roy. Soc.* xxi. 442) relate to those vegetable colouring matters, soluble in carbon sulphide and in non-volatile oils, which appear to be of the greatest importance to the life of plants. They are divided into seven groups, according to their origin, mode of occurrence, and spectroscopic appearances. Of these, the most important and most widely diffused is: (1). The chlorophyll-group, consisting of three substances, soluble in carbon sulphide, insoluble in water, exhibiting absorption at both ends of the spectrum, and distinct absorption-bands in the red; the strongest of which is related to the red fluorescence; decomposed more or less easily by acids into new products, the spectra of which are analogous to, but quite distinct from, those of the respective substances in their natural state; very quickly decomposed by direct sunlight in contact with the air. These three substances are: a. *Blue chlorophyll*, the most widely diffused of all plant-colours: it has a blue-green colour and three strong absorption-bands in the red, the least refrangible being the strongest of the three. The absorption at the blue end consists essentially of a broad black band between the blue and the violet, which can be seen only in a moderately pure solution, with very clear daylight. b. *Yellow chlorophyll*, which cannot be isolated, but is easily recognisable in association with the preceding. Its solution in benzene exhibits in the red an absorption-band somewhat further from the red end than the principal band of blue chlorophyll, and a second much fainter in the orange; there is also a broad and strong band in the middle of the blue, the whole of the blue being absorbed. With alcohol as a solvent, the absorption-bands of all these three bodies are shifted towards the more refrangible end of the spectrum, and the first band of yellow chlorophyll becomes broader, so that in mixtures it becomes confounded with that of the blue chlorophyll. c. *Chlorofucin*, occurring in fresh-water Algae, may be obtained in the pure state and of a yellow-green colour. Its spectrum shows two dark absorption-bands, one between the red and orange, another between the orange and yellow. The whole of the green is transmitted, but the whole of the blue is cut off, and when the solution is dilute, a broad and somewhat obscure band may be seen by very clear daylight in the centre of the blue. The fluorescence-spectra of these three substances are distinguished from one another still more clearly than the absorption-spectra, by a greater difference in the positions of the narrow bright red bands. The three members of the chlorophyll-group are decomposed with greater or less facility by acids, each giving rise to a different product, so that, though they have many generic properties in common, they must be regarded as well-marked species, and not in any way as mere accidental modifications of the same substance.

2. The Xanthophyll-group comprises a large number of substances, the following six of which are commonly met with in leaves or fronds or in fungi. They all exhibit two conspicuous absorption-bands in the green or blue, beyond which the spectrum becomes very faint; with alcohol as a solvent, these bands are shifted further towards the violet. The bands are not immediately altered by weak acids or alkalis; hydrochloric acid slowly decolorises the alcoholic solution. Light decomposes it more readily in proportion as the absorption-bands are more shifted towards the red end. The substances a to e are so arranged that the two absorption-bands in each one are shifted towards the violet end more than those in the one immediately preceding; in the first they are situated in the green; in the fifth at the green end

of the blue. a. *Phycoxanthin*: the solution in carbon sulphide has a fine crimson colour, the alcoholic solution is yellow. b. *Pezizaxanthin*: orange-yellow, obtained from *Peziza aurantia*. c. *Orange Xanthophyll*: a very widely diffused colouring matter; the solution in carbon sulphide has a faint reddish orange colour. d. *True Xanthophyll*: faint orange-yellow. e. *Yellow Xanthophyll*: obtained especially from yellow flowers; the solution in carbon sulphide is lemon-yellow. f. *Fucoxanthin*: the chief colouring matter of the olive-coloured Algæ; its solution in carbon sulphide has an amber colour; the spectrum is intermediate between those of c and d; alcohol produces much less increase of refrangibility in the bands; the substance is also less easily decomposed by light.

3. *Lichnoxanthin*-group: spectra without bands, but with more less extended absorption of the blue end; much less affected by light and by acids than the two preceding groups: a. *Orange Lichnoxanthin*: the absorption extends over the blue and green, and shades off as far as the yellow. b. *True Lichnoxanthin*: orange-yellow; the absorption ends suddenly in the middle of the green. c. *Yellow Lichnoxanthin*: the absorption does not extend quite so far into the green.

4. *Phycocyanogen*-group: Soluble in water. a. *True Phycocyanogen*, with a distinct absorption-band in the orange, and a narrow one in the red, imparting to the solution a very intense red fluorescence. b. *Crimson Phycocyanogen*: the chief absorption-band lies between the yellow and green; a second broad band exciting fluorescence in the orange.

5. *Phycerythrin*-group: soluble in water and non-fluorescent; a. *Crimson Phycerythrin* has an absorption-band at the yellow end of the green. b. *Red Phycerythrin* has an absorption-band at the blue end of the green.

6. *Erythrophyll*-group: soluble in water, insoluble in carbon sulphide; these bodies appear to be not essential constituents of leaves, but merely occasional products. Their number is considerable, but the conditions of their existence are as yet but little known; they are but slightly affected by light.

7. *Chrysotannin*-group: pale yellow aqueous solutions, slowly altered by light; their oxidation-products yield the autumnal yellow of leaves.

Crystallised Chlorophyll.—A. Gautier (in 1877) obtained pure crystallised chlorophyll by the following process. The green leaves of spinach and cresses are bruised in a mortar, with addition of sodium carbonate, so as to neutralise the acidity of the juice, and then pressed; the solid residue is suspended in alcohol of 55°, again pressed, and the process is repeated with alcohol of 83°, whereby chlorophyll, wax, fats, and pigments are dissolved. The liquid is then filtered, and shaken with pure animal charcoal, the green colouring matter being thereby absorbed after several days; the charcoal is washed with alcohol of 65°, which removes a yellow crystallisable substance, and then washed with dry ether, or light petroleum, whereupon the chlorophyll dissolves, and is deposited in dark-green crystals by slow evaporation.

Chlorophyll thus prepared forms needles about half a centimeter long, of soft consistence, and turning yellowish- or greenish-brown on keeping. Some of the smaller crystals transmit green light, and some lilac. The crystalline form appears to be an oblique rhomboidal prism, the rhombohedral angle being about 45°. Chlorophyll presents a striking analogy to bilirubin; it is soluble in the same solvents; it is removed from its solutions by animal charcoal, and may be recovered by treatment with ether or petroleum; it forms salts with bases; is easily oxidised in presence of light; undergoes numerous changes accompanied by alteration of colour; and combines directly with nascent hydrogen. When digested with hydrochloric acid, it splits up into phylloxanthin, a brown substance, crystallising from ether or hot alcohol, and Frémy's phyllocyanic acid, an olive-green substance, soluble in alcohol and ether, and forming salts with bases. Chlorophyll prepared as above is perfectly free from iron (Gautier, *Compt. rend.* lxxix. 861).

A crystallised substance, called 'chlorophyllane,' apparently identical with Gautier's crystallised chlorophyll, has lately been obtained, together with erythrophyll, by Hoppe-Seyler (*Ber.* xii. 1555) by treating grass-leaves previously freed from wax by digestion in ether, with hot alcohol. The analyses of the two substances by Gautier and Hoppe-Seyler give the following results:

	C	H	N	O	P	Mg	Ash	
Cryst. chlorophyll	73.97	9.80	4.15	10.33	—	—	1.75	Gautier
Chlorophyllane	73.4	9.7	5.62	9.57	1.37	0.34	—	Hoppe

Decoloration of Green Leaves in Bright Sunshine.—Experiments by J. Böhm (*Landw. Vers.-St.* xxi. 463) show that the green leaves of the scarlet runner, when exposed to bright sunshine, are first bleached, then become brown, and acquire a metallic lustre, and finally perish: further, that the underside of the leaf is much more sensitive to light than the upper.

On the Change of Colour of Leaves in Autumn, see Kraus (*N. Rep. Pharm.* xzii. 273; *Jahresb. f. Chem.* 1873, 842).

Alteration of the Colours of Flowers.—D. S. Martin (*Amer. Chem.* vii. 300) observes that the changes in the colours of the petals of certain flowers are in some way dependent upon atmospheric moisture. The petals of the dark blue variety of *Ipomœa purpurea* turned red in damp air, and when they were exposed to rain, sharply defined spots were formed upon them, red at first, but afterwards turning white. These changes are attributed by Martin, on the ground of special experiments, to an acid substance present in the air.

Diffusion of Plant-colours.—These colouring matters exhibit considerable diversity in their modes of diffusion when the organs containing them are immersed in a saturated solution of borax. The dissolved colouring matters diffuse rapidly, a red flower of *Antirrhinum majus* becoming in a few days transparent and colourless, like glass, whereas solid colouring matters, or those which are deposited in granular form, diffuse in a borax solution either very slowly or not at all; the common marigold (*Calendula officinalis*) retains the yellow colour of its flowers and the green of its leaves even when immersed in borax-solution for a year. When dissolved and granularly deposited colouring matters occur together in a plant, they may be separated by diffusion; thus the violet colour of *Iberis amara* diffuses quickly, giving place to a previously invisible greenish-yellow colour. The petals of *Pelargonium roseum* quickly lose their red colour by diffusion, and acquire a violet tint due to a granular colouring matter. The red leaves of a variety of *Atriplex hortensis*, which, according to Saussure's observations, give off oxygen like green leaves, also contain chlorophyll, the presence of which may be demonstrated by a diffusion experiment. The *Florideæ* likewise contain chlorophyll in addition to a red colouring matter which diffuses easily in borax-solution. The one-celled *algæ*, whether green or red, contain only granular colouring matters; the *Diatomacæ* contain an easily diffusible yellow colouring matter, *phylloxanthin*, together with chlorophyll. The roots of a fresh plant of *Lemna* dipped into the juice of *Phytolacca decandra* did not take up any of the colouring matter of that plant, but the colouring matter of a drop of fresh blood was readily absorbed by a leaf of *Drosera rotundifolia* (J. B. Schnetzler, *N. Arch. ph. nat.* lx. 388).

PLANT-MUCILAGE. The mucilage of quince-pips, linseed and fleabane seed, has been examined by Kirchner a. Tollens (*Liebig's Annalen*, clxxv. 205). To obtain it, the material was digested with water for four hours; the viscid mucilage thereby obtained was passed through a hair-sieve, then boiled, filtered through linen, concentrated by evaporation, acidulated, and precipitated with strong alcohol; and the precipitated mass was successively treated with acidulated and with pure alcohol, then repeatedly with ether, and finally dried over sulphuric acid.

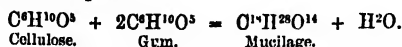
Quince-mucilage thus prepared is greyish-white and swells up, when soaked in water, to a gelatinous mass, forming a mucilaginous solution only on the addition of a small quantity of potassium hydrate. It still contains 4 to 5 per cent. of mineral matter, and on analysis gives numbers corresponding with the formula $C^{18}H^{28}O^{14}$. When it is boiled with dilute sulphuric acid, white flocks are precipitated, and sugar and dextrin or gum are produced. From the results of numerous carefully conducted quantitative experiments, it would seem that the flocculent precipitate of cellulose is nearly constant after the first half-hour, however long the boiling may be continued; but the percentage of gum gradually decreases, whilst that of the sugar increases within certain limits, showing the conversion of the former into the latter. The gum is optically dextrogyrate; the sugar, which reduces cupric solution, is dextrogyrate. The flocculent precipitate, amounting to about 36 per cent., gives with iodine the reactions of cellulose, but in the analysis the carbon comes out slightly higher than that required by the formula $C^6H^{10}O^5$. This is probably due to the presence of some impurity similar to the compound found in fir-wood by J. Erdmann (*ibid.* Suppl. v. 223).

Linseed-mucilage.—Linseed treated in like manner gave numbers corresponding with the formula $C^6H^{10}O^5$, or the same as that of cellulose. When boiled with dilute sulphuric acid, it decomposes like quince mucilage, but with much greater difficulty, gum and sugar being formed, and the former being gradually converted into the latter by long-continued boiling. The insoluble residue is very much smaller than with quince mucilage, being only about 4 per cent.

Fleabane-mucilage has the formula $C^6H^{10}O^5$. Boiled with acids, it decomposes like the other mucilages, yielding gum and sugar, but in this instance, by long-continued boiling, the gum is completely converted into dextrorotatory sugar.

From these results it is inferred that in quince mucilage the cellulose exists in combination with the gum, since no cellulose can be distinguished as such by micro-

scopical examination; and as the two substances exist in the ratio 1 : 2, it is most probably a true chemical compound :—



It has yet to be determined whether the other two mucilages are distinct, or whether they are compounds of cellulose and gum in the proportion 1 : 2, mixed with excess of gum : the different behaviour of the fleabane mucilage when treated with acid from that of the quince would, however, seem to preclude this view.

PLANTS, RESPIRATION AND NUTRITION OF. *Formation of Oxygen by Leaves.*—From experiments by J. Boehm (*Ber.* vi. 550), it appears that the formation of oxygen by green leaves immersed in carbonic acid water does not result from the direct assumption of absorbed carbon dioxide by the chlorophyll-bearing cells, but that the leaves first become covered with an atmosphere containing carbon dioxide, and then act as under normal conditions. This conclusion is based upon the following facts : 1. Leaves of *Juglans* and other plants immersed in water containing carbonic acid, give off but little gas on exposure to sunshine if the bubbles which form on them are removed as soon as they appear. 2. The evolution of gas ceases when the absorption-coefficient of the water for carbon dioxide is increased by lowering of temperature or increase of pressure, whereas gaseous CO^2 is decomposed under similar conditions. 3. The separation of gas likewise ceases if the leaves before the experiment are injected with water, and the conditions which induce the formation of bubbles upon them are thereby lowered. Injected leaves of land-plants, however, when placed in an atmosphere of carbon dioxide, still give out a large quantity of oxygen.

Experiments on the decomposition of carbon dioxide by the green leaves of land-plants, in mixtures of that gas with hydrogen, showed that the quantity of oxygen produced is always greater than that of the carbon dioxide which disappears. This excess is due to the fact that the living tissues of land-plants, placed in an atmosphere free from oxygen, continue to give off carbon dioxide as long as they live, the quantity of that gas thus evolved depending especially on the temperature. This evolution of carbon dioxide by living plants in an atmosphere free from oxygen is regarded by Boehm as analogous to the processes which may be observed in beer-yeast, especially in its spontaneous fermentation, the organisms excluded from access of oxygen then acquiring the forces necessary for their vital processes by 'internal combustion.'

Experiments by Boehm (*Liebig's Annalen*, cxxxvi. 248) on the elimination of oxygen from green twigs under boiled water in sunlight have led to the following results :

1. When green twigs of woody plants, such as privet, are enclosed in a limited atmosphere containing oxygen, in the dark, there ensues at first a diminution, but afterwards an increase, in the volume of the enclosed gases; and this increase takes place before the oxygen present is completely absorbed.

2. The diminution in the volume of gas which takes place when green twigs are enclosed in an atmosphere containing oxygen, in faint light, is not due to assimilation of oxygen, as in the germination of seeds rich in oil, but is caused by absorption of carbon dioxide formed in normal respiration.

3. When portions of fresh plants are enclosed in an atmosphere of carbon dioxide, there takes place at first a diminution (contrary to Saussure's statements) and afterwards an increase in the volume of the gas, due to internal respiration.

4. The absorption of carbon dioxide by fresh plants is not due to the action of cellular liquids (*Zellsaft*) exclusively, since it takes place also in twigs previously dried at 100° .

5. When fresh green shoots of privet are exposed to sunlight, under boiled water, they give off more oxygen than corresponds with the volume of air contained in them. This oxygen is for the most part derived from carbon dioxide formed in the shoots by internal respiration. In prolonged experiments the evolution of oxygen becomes slower and slower, and after 3 or 4 days ceases entirely, although the shoots still appear fresh and sound. After a week, however, the shoots begin to turn brown, and butyric fermentation sets in.

Certain fleshy plants, as *Bryophyllum calycinum*, *Crassula arborescens*, *Sempervivum Cotyledon*, when exposed to light, give off oxygen even in an atmosphere free from carbon dioxide, this effect being due to the deoxidation of an organic acid (probably an isomeride of malic acid); in several experiments, the juice of the plants, after the elimination of oxygen, was found to be slightly alkaline. Leaves of *Bryophyllum* and *Crassula* kept in the dark till nearly all their starch had disappeared, and then exposed to light in an atmosphere free from carbon dioxide, again became charged with starch, whence it may be inferred that the reducible acid was in this

case converted into a carbohydrate (A. Mayer, *Ber.* viii. 1088; *Landw. Vers.-St.* xxi. 277).

Absorption of Oxygen, and Formation of Carbon Dioxide.—The observation that green leaves in the dark take up oxygen and give off carbon dioxide, and that the amount of CO_2 thus given off increases with the temperature, has been confirmed by Dehérain and Moissau (*Compt. rend.* lxxviii. 1112). They find that the volume of carbon dioxide given off, especially at low temperatures, is less than that of the oxygen absorbed, and thence infer that this part of the absorbed oxygen is used for the formation of oxalic and other vegetable acids. Finally, they show that the leaves still continue to give off carbon dioxide, even after all the oxygen of the surrounding atmosphere has been removed.

Corenwinder (*Compt. rend.* lxxxvi. 608) observes that young leaves take up oxygen and give out carbon dioxide even in daytime, whereas old leaves give off no carbon dioxide during the day. Cherry-laurel leaves dried at 100° were found to have the following composition:

	Young leaves	Old leaves
Nitrogenous constituents	32.47	10.75
Non-nitrogenous constituents	61.89	81.69
Phosphoric acid	1.68	0.35
Lime	0.86	3.80
Potash, silica	3.00	3.41

The young leaves, in consequence of their large amount of protoplasm, absorb oxygen and exhale carbon dioxide; the old leaves, on the other hand, contain comparatively little protoplasm, but a large quantity of chlorophyll, which retains and decomposes the carbon dioxide produced by the respiration of the protoplasm, so that oxygen is evolved.

In the respiration of water-plants in atmospheric air, less oxygen is consumed than in the respiration of land-plants under similar circumstances. In an indifferent atmosphere free from oxygen, carbon dioxide is formed by water-plants, but in smaller quantity than by land-plants. Dead water-plants absorb hydrogen gas in considerable quantity, apparently in consequence of a peculiar kind of fermentation. In land-plants this absorption of hydrogen has not been observed (Boehm, *Ber.* viii. 752).

According to Mercatante a. Colossi (*Gazz. chim. ital.* 1875, 32), no carbon dioxide is eliminated from the roots of plants, so long as they remain in normal condition, this elimination commencing only when the actual decomposition of the roots begins. Hence they infer that the carbon dioxide taken up by the leaves bears no relation to that given off from the roots; that the carbon dioxide occasionally given off by the roots has no appreciable influence on the solubility of the constituents of the soil; and that, on the other hand, the organic constituents of the soil do not act on the dissolved organic constituents in such a manner as to render them insoluble and incapable of absorption by the roots of plants.

Respiration in the Ripening Fruits of Poppy and Rape.—The amounts of oxygen consumed and of carbon dioxide evolved by poppies and rape at various stages of ripeness have been determined by Sabanin a. Laskowsky (*Land. Vers.-Stationen*, xxi. 194), flowering stems cut as short as possible being used for the purpose. The results are given in the following table, where the numbers in the first column indicate the order of ripeness, No. I in each case being a flowering-stem taken just after flowering, No. VII in the rape-series a stem bearing fully-ripened seed-pods, and No. VIII in the poppy-series an over-ripe capsule. The last four columns give the weight in milligrams of oxygen consumed and carbon dioxide formed in 24 hours by 1 gram of dry substance.

	Rape		Poppies	
	Oxygen	CO_2	Oxygen	CO_2
I . . .	65	89	91	124
II . . .	70	97	30	42
III . . .	37	51	24	33
IV . . .	14	19	24	33
V . . .	16	22	23	31
VI . . .	20	27	20	28
VII . . .	12	16	15	21
VIII . . .	—	—	8	11

It appears from these results that in both plants the consumption of oxygen falls off as the fruit ripens. From what is known of the disappearance of starch in these plants, it may be inferred that the maximum consumption of oxygen occurs just before the disappearance of starch.

Elimination of Hydrogen from Plants.—According to Selmi (*Gazz. chim. ital.* 1875, 32), mildew and larger fungi give off hydrogen, especially on the side turned away from the light; in most cases the hydrogen is burnt by the oxygen of the air, and part of it unites with atmospheric nitrogen, forming ammonia. Missaghi, on the other hand (*ibid.* 419), finds that the air surrounding a growth of mildew contains no free hydrogen. Müntz (*Compt. rend.* lxxx. 178) observes that the common mushroom (*Agaricus campestris*), in an atmosphere containing oxygen, gives off nothing but carbon dioxide, whereas in an atmosphere free from oxygen, e.g. in nitrogen or carbon dioxide, hydrogen is likewise eliminated; the agaric is then found to contain alcohol, and Müntz supposes that, under these conditions, the mannite contained in it is converted, with separation of hydrogen, into glucose, which is further split up into carbon dioxide and alcohol. The same reaction was found to take place in beer-yeast.

According to Pollacci (*Gazz.* 1875, 451; 1876, 258; *Ber.* ix. 84), hydrogen is evolved not only from fungi, but from all plants, and in the case of sulphured vines this hydrogen gives rise to the formation of hydrogen sulphide, which kills the *oidium*. The evolution of hydrogen is most abundant on those parts of the plant at which vegetation is most active.

Absorption of Nitrogen.—A comparison made by Grandea (*Iust.* 1875, 110) of the researches made in late years on the origin of the Nitrogen of Plants, points to the conclusion that the soil does not possess the power of bringing the nitrogen of the atmosphere into a form in which it can be assimilated by plants, and that the nitrogen in the soil which is capable of assimilation is of animal or vegetable origin.

G. Villes (*Chem. News.* xxx. 278, 287) infers from experiments in which soils were manured with various nitrogen and phosphorus compounds, viz. nitrites and nitrates, ammonia, methylamino, ethylamine, urea, ethyl-urea, tetramethylammonium chloride, oxamide, dimethyloxamide, diethyloxamide, potassium cyanate, ammonium oxalate, phosphates, phosphites, and hypophosphites,—that the produce depends not only on the quantity of nitrogen and phosphorus employed for manuring, but also very materially on the mode of combination in which these elements are present. See also C. A. Cameron (*ibid.* xxxi. f).

Absorption of Ammonia.—Experiments with various plants have been made by A. Mayer (*Landw. Vers.-St.* xvii. 329), with the view of determining whether ammonia is absorbed by the aerial parts of plants. For this purpose, ammonia was presented to the plants, partly in the gaseous form, partly in solution as ammonium carbonate, while the roots received none. The experiments led to the following conclusions: (1). Plants of the higher orders are capable of absorbing ammonia presented to their green organs, either in the gaseous form or as carbonate dissolved in water. (2). This absorption of ammonia is not purely mechanical, but leads, under favourable circumstances, to a physiological action; it is, in fact, a form of assimilation of nitrogen. (3). The nutrition of a plant by ammonia thus absorbed may, in the absence of other nitrogenous food, be followed by luxuriant growth, and an increased production of organic substance. (4). Green plants in all their organs are affected by ammonium carbonate in very different degrees, and if the supply of it be too great, the parts of the plant affected by it may die off. In the case of very sensitive plants, therefore, the demonstration of the assimilation of ammonia may be very difficult or even impossible. The absorption of ammonia from the atmosphere by leaves is theoretically possible, but considering the extremely small proportion of ammonia in the air, this source of supply cannot be regarded as of much practical importance. *Papilionaceous* plants, which are generally thought to take up more ammonia from the air than other plants, were found in the experiments above described to be particularly sensitive to and injured by it, though of course they might absorb it in very dilute form.

Experiments on the absorption of atmospheric ammonia by the leaves of plants have also been made by Th. Schloesing (*Compt. rend.* lxxviii. 1700). Two tobacco-plants were grown under similar circumstances, excepting that one of them developed its leaves in air containing ammonium carbonate, the other in air free from ammonia. The experiment lasted about six weeks, at the end of which time the leaves, buds, stalks, and roots were separately collected, dried, weighed, and analysed. The plant grown in the ammoniacal atmosphere contained 2.32 per cent., that grown in the non-ammoniacal atmosphere only 1.77 per cent. nitrogen. Of the total quantity of ammonia which had access to the leaves, three-fourths was absorbed. The ammonia had no influence on the amount of nicotine in the plant.

Absorption of Alkali-salts.—Peligot (*Compt. rend.* lxxvi. 1113) has made

experiments on the growth of beans, with the view of determining whether sodium-salts are taken up by plants from the soil. The plants were grown in good garden-mould, and those in the several pots were watered with different liquids, viz. snow-water, and solutions of sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, and magnesium-ammonium sulphate. The analysis of the ash of the full-grown plants showed that neither of them had taken up a sodium salt from the soil. The ashes of the plants which had been watered with potassium salts were not richer in potassium than those which had been watered with ordinary water.

Interchange of Potassium and Sodium in Plants.—Champion a. Pellet (*Compt. rend.* lxxx. 1588) infer, from a series of ash-analyses, that potassium and sodium can replace one another in plants in the ratio of their atomic weights.

Absorption of Water and Calcium-salts by the Leaves of the Scarlet-runner (Phaseolus multiflorus) (J. Boehm, *Landw. Vers.-St.* xx. 51).—Cotyledons of this plant containing starch may often be dried to a fourth, or even a fifth of their original weight, without entirely losing the power of producing and decomposing carbonic acid when placed in an atmosphere of pure hydrogen. The cotyledons, even when dried to about half their original weight, will recover their freshness if immersed, with the exception of the stems, in water. Leaves that have been thus revived, dry on exposure to the air much more quickly than freshly cut ones.

Scarlet-runner seedlings, the roots of which have been carefully wrapped in damp cloths, the leaves, however, being suffered to dry by exposure to the air, until each appears not more than half its former weight, do not revive when placed underneath a bell-jar with their roots immersed in water. They revive completely, however, when immersed, with the exception of the roots; when, therefore, a certain point is reached, the water necessary for their recovery can be taken up by the leaves only, and not by the roots. If a seedling be cut so that only the two cotyledons remain upon the stem, and one of these be dipped beneath the surface of water whilst the other is kept exposed to the air, the leaf out of the water will remain quite fresh; but if both leaves be allowed to dry before the one is immersed, the other will not again revive.

Seedlings of *Phaseolus multiflorus* possess the property of absorbing through their leaves not only water, but also the lime salts necessary for their development. Carbolic acid, in the proportion of 1 pt. per 1,000, can be added to the water used for their nourishment, without hindering growth.

Absorption of Bicarbonates.—Observations on the absorption of bicarbonates by plants from natural waters have been made by A. Barthélemy, with the following results:

1. Plants possess one set of roots for the absorption of gas, and another set for the absorption of mineral substances in solution.
2. There are two distinct periods in the life of the roots; of development, previous to the decrease of the bud; and of maturity, when the spongiole, laid bare by the exfoliation of the epidermic tissue, exhibits the phenomena of osmose.
3. Plants absorb more water than bicarbonates from natural waters, except when the leaves dry rapidly, or at the time of flowering.
4. The amount of bicarbonates absorbed is proportional to the amount of exhaled water.
5. In a water of constant composition, plants appear, during the night, to part with some of the bicarbonates absorbed during the day, while absorption of water takes place.
6. The proportion of the bicarbonate to the water absorbed varies with the nature of the plant.
7. When a plant has absorbed a certain amount of bicarbonates, it is able to part with some when placed in distilled water.
8. The absorption of bicarbonates has no direct relation to the rapidity of vegetation: this absorption therefore does not aid respiration.
9. The roots of plants reject the carbon dioxide which serves to keep the bicarbonates in solution.
10. These experiments made with healthy plants growing under normal circumstances coincide in many points with those made with concentrated solutions and in porous vessels.

Influence of various Substances on the Germination and Growth of Plants.—1. Of Carbon Monoxide. Young sprouts raised in an atmosphere of pure carbon monoxide, or of air containing 3 to 4 per cent. of that gas, or of air, hydrogen and carbon monoxide, soon became sickly, and died on the tenth or eleventh day. Hence it would appear that Baeyer's hypothesis (*Ber.* iii. 63) respecting the formation of sugar in plants by reduction of CO_2 to CO, the combination of the latter with hydrogen to COH_2 , and the subsequent condensation of this aldehyde, cannot be maintained (A. Stutzer, *Ber.* ix. 1570).

2. Of Coal-gas. See p. 543.

3. Of Ammonium Thiocyanate. O. Kohlrausch (*Dingl. pol. J.* cxxii. 425) manured a turnip-field, and a garden soil in which barley and summer-wheat were sown, with ammonium sulphate containing 2.52 per cent. thiocyanate obtained from

spent Laming's mass (mixture of lime, ferric chloride, and sawdust, used for the purification of coal-gas). In all cases the germination of the seeds was retarded, and the plants were very ill-developed, the effect being most marked with the wheat. Similar results have been obtained by C. Schumann (*Landw. Vers.-St.* 1872, 230; and P. Wagner, *Zeitschr. für die landwirthschaft. Vereine d. Grossherzogthums Hessen*, 1873).

4. Of Alkalis. Böttger (*Dingl. pol. J.* ccxii. 444) finds that moderately strong solutions of potassium or sodium hydrate greatly increase the germinative power of seeds, especially of coffee-beans, which, when drenched with a weak solution of caustic potash, throw out long white radicles even in an hour or two.

5. Of Lime. Boehm (*Ber.* viii. 682) found that seeds of the scarlet-runner, if allowed to germinate in distilled water, die sooner or later when the reserve of nourishment is exhausted, although the length of time required for this varies greatly in individual plants. This effect is prevented, however, by the presence of various calcium salts (not by calcium chloride), but no other base can be substituted for lime, magnesium carbonate acting in a decidedly injurious manner. Boehm is of opinion that lime plays a similar important part in the development of plant-life that it does in the animal economy in the transformation of cartilage into bone; but that its action in causing the transfer of starch from the parts of the plant where it is stored up to those in which it is utilised is obscure.

6. Of Salicylic acid and Thymol. According to E. Heckel (*Compt. rend.* lxxxvii. 613), germination is retarded and in some cases entirely prevented by the presence of salicylic acid, sodium salicylate, or thymol.

7. Of Camphor. The growth of many plants is accelerated by camphor, but on others it exerts either a deleterious influence or none at all. It accelerates germination. A similar influence is exerted by water containing oil of turpentine (Vogel a. Kaab, *Pharm. J. Trans.* [3], iv. 1014).

8. Of Oils. Noble a. Hanlein (*Landw. Vers.-St.* xxi. 437) have made experiments on the influence exerted on vegetation by various volatile oils, especially those of lavender and curled mint, also by benzene and carbon sulphide, these liquids having been recommended for the destruction of the Phylloxera and of the Colorado beetle. The experiments showed that all these liquids exert a deleterious action on plants. Carbon sulphide is very efficient in destroying underground insects and larvae, but its action on plants is even more destructive than that of any of the other liquids just mentioned.

Chemical Changes accompanying Germination. The observations of Schulze, Umlauf a. Urich on the transformations of tissue attending the germination of lupine-seeds have already been noticed (p. 1243). Further experiments on the formation of sulphuric acid in germination have been made by Schulze (*Ber.* xi. 1234). Vetch-sprouts which had been growing in the dark for three weeks were found to contain a larger quantity of sulphates than the ungerminated seeds, the amount of sulphuric acid produced being about equal to that which could be formed from the sulphur of the decomposed proteids. An increase of sulphates takes place also in the germination of pumpkins. In the case of lupine sprouts of various ages it was found that in the first stages of germination the agreement between the quantity of sulphur separated from the decomposed proteids and the amount of sulphuric acid formed does not exist, but the greater the age of the sprouts, the more completely is this agreement established. This result may be explained on the supposition that the proteids are first split up under the influence of ferments, and that the products of the decomposition then undergo gradual oxidation. In the later stages of germination, the amount of sulphuric acid appears to afford a measure of the quantity of albuminoid matter decomposed.

According to Schulze a. Barbieri (*Ber.* x. 928; xi. 710), pumpkin-sprouts contain an amide of glutamic acid, together with aspartic acid, tyrosine and leucine. The process of decomposition of albuminoids in germination is therefore the same as that which takes place under the influence of acids.

Formation of Carbohydrates in Plants.—Experiments have been made by A. Stutzer (*Ber.* ix. 1395) on sprouts of *Brassica Rapa*, growing in nutritive solutions to which oxalate or tartrate of calcium had been added, the air of the vessel having been previously deprived of carbon dioxide. Under these circumstances the plants took up oxalic or tartaric acid in place of atmospheric carbon dioxide, formed new leaves, and increased in amount of dry substance. Water-plants growing in similar nutritive liquids gave off in sunshine considerable quantities of oxygen. When the conditions of the experiment were modified so that the air surrounding the plants was kept free from carbon dioxide during the whole course of the experiment, the oxalic acid was not assimilated, the plants soon died, and their dry weight was diminished. It follows, therefore, that oxalic acid—contrary to Liebig's view—cannot be regarded

as a transition-member between atmospheric carbon dioxide and the carbohydrates, but that, before it can take part in the process of nutrition, it must be oxidised to carbon dioxide. With tartaric acid, however, the case is different; for plants grow in a nutritive solution containing this acid even though surrounded by an atmosphere free from carbon dioxide, the two alcoholic groups CH^2OH in the tartaric acid serving as nutriment to the plant. Glycerin acts in the same manner as tartaric acid. These results show that carboxyl-groups, COOH , cannot serve directly for the formation of vegetable substances in plants containing chlorophyll under the influence of light, but only after oxidation; alcoholic groups, on the other hand, are directly available for this purpose. When the nutritive liquids contained acetates or succinates the plants increased in dry substance, and threw out new leaves, but they never looked so vigorous as those which were fed with tartaric acid.

Formation of Starch in the Chlorophyll-granules.—Experiments by J. Boehm (*Ber.* ix. 123) on the shortest time in which, under favourable conditions, starch is formed in the chlorophyll-granules, have led to the following results: 1. The view hitherto held, that all starch which makes its appearance in chlorophyll-granules free from starch, when these are exposed to full daylight, is a product of the direct assimilation of carbon dioxide, is erroneous. 2. Light of any intensity sufficient to enable green plants to decompose carbon dioxide, effects also a transfer of starch from the stems to the chlorophyll-granules. 3. In direct sunshine the transfer of a recognisable quantity of starch from the stems to the chlorophyll-granules of the leaves takes place in 10 or 15 minutes. 4. Experiments on the formation of starch in the chlorophyll-granules, consequent on the direct assimilation of carbon dioxide, can be made only with plants perfectly free from starch, or with detached leaves freed from starch. 5. The disappearance of starch in detached leaves in diffused daylight or in the dark takes place as rapidly as in leaves still attached to the plant. The starch in leaves not very rich in starch disappears also when such leaves are partially or entirely immersed in water in large open vessels, but not in water free from oxygen, or in pure nitrogen or in hydrogen. 6. Detached leaves of plants grown in faint light, and free from starch, when placed in an atmosphere containing 6 or 8 per cent. of carbon dioxide in full daylight, not only throw out roots from the leaf-stalks, but also increase considerably in diameter, even when simply moistened with distilled water. 7. Quite young cotyledons grown in the dark, or in faint light, contain starch. 8. Sprouts grown in distilled water, under bell-jars standing in potash-ley, scarcely attain the length of 10 cm., the stems then withering below the cotyledons. Such plants are, as a rule, destitute of starch. 9. Starch is formed in recognisable quantities in 10 or 15 minutes, by detached cotyledons, when exposed to direct sunshine in an atmosphere containing 8 per cent. of carbon dioxide. In similar leaves, freely exposed to the air, in sunshine, the same result occurs in 45 minutes. It is not improbable that the carbon of the dioxide decomposed combines directly with water to form starch. 10. Scarlet-runner sprouts take up from the soil neither organic carbon-compounds nor carbon dioxide.

Further experiments (*Ber.* x. 1804) have shown that the formation of starch in chlorophyll-granules free from that substance, at the expense of substances which have been transferred to the cells containing these granules, is a process of the organism perfectly independent of the influence of light. When growing cotyledons of the scarlet-runner, the terminal buds of which have been removed at an early stage, are partly shaded, the starch at first disappears almost wholly from the darkened parts of the leaves, but after two or three weeks the chlorophyll-granules in the parenchyma cells of the shaded parts are always found to contain starch, sometimes equal in quantity to that which would have been formed if they had been continuously exposed to light. Hence it appears that the starch which is formed in chlorophyll-granules previously free from that substance is not in all cases a direct product of assimilation of carbon dioxide and water, but may be formed from substances previously assimilated and transferred to the cells.

On the formation of Starch in the cotyledons of Cress, Radish, and Flax, see Boehm (*Chem. Centr.* 1875, pp. 202, 217, 233, 248; *Jahresb. f. Chem.* 1875, 817; *Chem. Soc. J.* xxix. 952).

Albinism in Plants.—The difference in composition and function between white and green leaves has lately been carefully studied by A. H. Church (*Chem. Soc. J.* 1879, xxxv. 33; 1880, xxxvii. 1). The leaves examined were those of a species of maple, *Acer Negundo*, the variegated holly and ivy, also of the following exotic plants: *Eleagnus pungens*, *Plectogone variegata*, *Cyperus alternifolius* and *Alocasia macrorrhiza*. The white leaves and white parts of leaves of these plants were found to contain about 5.58 per cent. more water than the green; they also yielded a larger proportion of ash, and this ash was richer in potash and poorer in lime than that of

the green leaves; in short, the white leaves contain a larger proportion of the more diffusible constituents. Moreover the white foliage, which contains no chlorophyll, does not possess the power of decomposing the carbon dioxide of the air, even in sunshine, but on the contrary adds largely to the normal amount of that gas in the air, acting indeed like the petals of flowers and like green leaves in darkness. In all these respects the white foliage of a plant bears to the green the same relation that a parasitic plant bears to its host, *e.g.* the dodder to the clover on which it grows. It does not elaborate its own substance; it is not a laboratory, but merely a storehouse, and draws the whole of its sustenance from the green parts of the plant in which the functions of vegetable life are in full activity. Remarkable differences are also observed in the amount of gain and loss of white and green foliage when placed in water and when exposed to the air. White holly sprays placed in water gained in two hours 0·29 per cent. of their weight; green holly under similar conditions gained 1·55 per cent. When no water was supplied, the white holly lost 0·54, the green 10·26 per cent. of its weight.

PLATINUM. *Occurrence.*—A specimen of magnetic platinum ore from Nischne-Tagilsk, in the Ural, analysed by Terroil (*Compt. rend.* lxxxii. 1116), was found to contain:

Platinum, with traces of Iridium	81·02
Osmiridium and other platinum-metals insoluble in aqua regia	3·33
Silver	traces
Copper	3·14
Iron	8·18
Nickel	0·75
Chrome-iron ore	3·13
Silicon	0·13
Silicates of Aluminium, Magnesium, and Iron	traces
	99·68

The occurrence in this ore of metallic iron and nickel, which had not hitherto been found in platinum ore, indicates a resemblance between platinum ores and meteorites. On this point see also Daubr e (*Compt. rend.* lxxx. 707; *Jahresb. f. Chem.* 1876, 1194).

Ferruginous platinum from Russia, analysed by Frenzel (*Jahrb. f. Min.* 1874, 684), gave:

Pt	Fe	Cu	Insoluble	Sp. gr.
76·97	10·97	1·04	1·45	14·92 at 15°.

The following table gives the results of the analysis of Russian platinum ores by S. Kern (*Chem. News*, xxxv. 88). 1-3. From the District of Goroblagodatsky. 4-6. From the District of Nischne-Tagilsk:

	Pt	Rh	Ir	Os	Pd	Fe	Cu	Osmir- idium	
1.	87·50	1·20	0·05	0·01	1·05	8·60	0·85	1·50	= 100·56
2.	84·50	2·90	0·90	0·60	0·05	7·55	0·60	2·80	= 99·90
3.	80·05	1·05	2·50	trace	2·03	11·04	1·02	2·51	= 100·20
4.	80·87	4·44	0·06	trace	1·30	10·82	2·30	0·11	= 99·90
5.	71·20	1·50	2·40	0·05	1·95	13·40	6·70	2·65	= 99·85
6.	89·05	4·60	trace	trace	2·35	3·40	0·59	trace	= 99·89

Also traces of Ruthenium.

Preparation.—Th. Kn sel (*Ber.* vi. 1159) separates platinum from the residues obtained in the use of platonic chloride for the estimation of potassium, by heating these residues with sodium or potassium carbonate, or sodium hydrate, in a porcelain dish over the water-bath, and gradually adding the alcoholic wash-waters. The spongy platinum thereby reduced is washed, dried, and finally boiled with hydrochloric acid to separate any remaining impurities. Duvallier (*Compt. rend.* lxxxiv. 444) effects the reduction of the platinum from these residues by boiling them with an alkaline formate.

On the separation of Platinum from the Ferric Chloride obtained in the preparation of Fine Gold, see Opificius (*Dingl. pol. J.* ccxxiv. 414; *Jahresb. f. Chem.* 1877, 1124).

On the separation of Platinum from Rhodium, Iridium, and Osmium by precipitation with Mercaptan, see p. 1276.

The method of working native platinum, practised at Her us' works in Hanau, is described by J. Philipp (*Dingl. pol. J.* ccxx. 95; *Jahresb. f. Chem.* 1876, 1075; *Chem. Soc. J.* xxx. 176).

Reduction.—According to Pellet (*Compt. rend.* lxxvii. 112), platinum is reduced from the solutions of its salts by hydrogen containing a trace of arsenic, but not by pure hydrogen.

Platinum-black.—According to Zdrawkowitch (*Bull. Soc. Chim.* [2], xxv. 198), a platinum-black of great catalytic power may be prepared by reducing platinum with glycerol in alkaline solution. A good mode of proceeding is to mix 15 c.c. glycerol of 25° to 27° B. with 10 c.c. potash-ley of sp. gr. 1.08, heat the mixture to boiling, and add 3 to 5 c.c. of ordinary solution of platinic chloride, whereupon the platinum is almost instantly separated as a black flocculent or pulverulent precipitate. If a large excess of alkali is used, the platinum is thrown down in specular form. Platinum is likewise reduced from the ordinary acid solution of platinic chloride by boiling with glycerol; but the reduced platinum thereby obtained is rather grey than black, and has but little activity.

Alloys. 1. With Iron. From synthetical experiments, as well as from the analysis of native alloys, of platinum and iron, Daubree finds that polar magnetism is exhibited only by those which contain at least 17 per cent. iron, those with lower percentages of iron being susceptible of magnetism, but not exhibiting polarity (*Compt. rend.* lxxx. 526). See also Deville (*ibid.* 589).

A portion of a sulphuric acid condenser of platinum, which was brittle and crystalline throughout, was found by E. Beichardt (*Dingl. pol. J.* ccciii. 445) to contain 99.430 per cent. platinum, 0.473 copper, 0.013 iron, and 0.030 silicon.

2. With Iridium. G. Matthey (*Chem. News*, xxxix. 175) has described the methods by which he prepares an alloy of iridium and platinum suitable for the manufacture of the international meter and kilogram standards, and of the geodesic rule.

Preparation of Pure Platinum.—Ordinary commercial platinum is melted with six times its weight of pure lead; the alloy, after granulation, is treated with successive quantities of dilute nitric acid (1 to 8) until there is no more action; and the solution, which contains lead, iron, copper, palladium, and rhodium, is separated from the residue and treated by appropriate methods. The residue, an amorphous powder containing platinum, lead, crystalline iridium, and small proportions of other metals, is treated with weak aqua regia, which dissolves the platinum and lead, leaving the whole of the iridium in an impure state. The solution is evaporated, the lead removed by sulphuric acid, the platinum solution is again evaporated, and the platinum chloride dissolved in water and mixed with an excess of ammonium and sodium chlorides. The solution, kept at 80° for several days, deposits the ammonium platinochloride, which is removed, and after being washed with saturated ammonium chloride and then with hydrochloric acid, is dried; and as it may still contain rhodium, it is mixed with potassium-hydrogen sulphate and a little ammonium-hydrogen sulphate, and gradually heated to dull redness in a platinum capsule. The platinum is thereby reduced in the form of a black powder, the rhodium then remaining as rhodium and potassium sulphate, which is completely dissolved out by digestion with boiling water; the solution contains also a little platinum, which is recovered by evaporating to dryness and heating the residue to redness, at which temperature the platinum salt alone is decomposed. The absolutely pure platinum obtained by this process has a density of 21.46.

Preparation of Pure Iridium.—The iridium obtained from an ordinary solution of this metal (freed from osmium by long boiling in aqua regia), by precipitation with ammonium chloride, contains traces of platinum, rhodium, ruthenium, and iron; the presence of platinum is unobjectionable when iridio-platinum is to be prepared. This iridium is fused for some hours with ten times its weight of lead; the lead dissolved out from the alloy by nitric acid; the residue subjected to a prolonged digestion with aqua regia; and the crystalline mass which remains is fused at a high temperature with potassium bisulphate in order to remove rhodium. The partially purified iridium is next melted for some time with 10 pts. of dry potassium hydrate and 3 of nitre in a gold crucible. The mass treated with cold water furnishes a solution containing potassium ruthenate and a 'blue residue' of potassium iridiate, which is washed with water containing potassium hydrate and sodium hypochlorite until the washings are colourless; then with distilled water; and then mixed with a solution of sodium hypochlorite and left at rest for some time. The mixture is next transferred to a retort, warmed, and finally boiled until the distillate no longer imparts a red colour to weak alcohol acidulated with hydrochloric acid (ruthenium). To remove the last trace of ruthenium from the residue, the treatment with nitre and potash and with sodium hypochlorite is repeated. The blue powder is then dissolved in aqua regia; the solution evaporated to dryness; the residue dissolved in distilled water; and the solution is filtered and poured slowly into concentrated solution of

soda containing sodium hypochlorite (no precipitate should be formed), which is then subjected in a distilling apparatus to a current of chlorine, the distillate being tested for ruthenium. The blue oxide of iridium precipitated by the chlorine is collected, washed, dried, and reduced in a glass tube by a current of the mixed gases (CO and CO²), obtained by gently heating a mixture of oxalic and sulphuric acids. The metallic iridium is heated to redness with potassium bisulphate to remove unreduced oxide of iron and traces of rhodium, and the insoluble portion, after many washings with water, is washed with chlorine-water to remove traces of gold, and with hydrofluoric acid to free it from silica. The remaining iridium, after calcination in a charcoal crucible, is melted to an ingot, which, after being broken up and boiled with hydrochloric acid to remove adhering iron, should, if perfectly pure, be of sp. gr. 22.39. The purest iridium prepared had a density of 22.38, and still contained almost inappreciable traces of oxygen, rhodium, ruthenium, and possibly iron.

Alloy of Iridio-platinum.—450 ounces of platinum and 55 ounces of iridium were melted together; and the resulting ingot was cut into small pieces by hydraulic machinery, then remelted and forged at a white heat under a steam hammer (the surfaces of which were cleaned and highly polished after each series of blows); passed through polished steel rollers; cut into narrow strips; and again slowly melted in a properly-shaped mould. This ingot, forged into a bar 35 cm. × 7.5 cm. × 2.5 cm., showed at zero a density = 21.522; after a second forging and rolling, the density was 21.648. After the bar had been passed through highly polished rolls until the dimensions were 40.80 cm. × 21 mm. × 5 mm., a perfectly rectangular form was given to it by drawing through a series of plates. The rule thus prepared for polishing had a density = 21.516, and gave on analysis:—

Platinum	89.40	89.42
Iridium	10.16	10.22
Rhodium	0.18	0.16
Ruthenium	0.10	0.10
Iron	0.06	0.06
		99.90	99.96

The density calculated from the first analysis is 21.510, and from the second, 21.515, which coincides with the actual determination.

The rule thus prepared for the *Association Géodésique Internationale* was perfectly free from flaws, susceptible of a splendid polish, and much more suitable than platinum for the dividing process.

Iridio-platinum possesses the following advantages for standard rules and weights: It is almost indestructible, has extreme rigidity, especially in the tube form, and a most beautifully polished surface can be obtained; its coefficient of elasticity is very great and its density very high. For weights, the alloy should contain not less than 20 per cent. of iridium. Such an alloy, sp. gr. 21.614, has a coefficient of elasticity = 22.2, one of the highest known, whilst its malleability and ductility are almost without limit. The kilogram prepared from it measures only 46.266 c.c., displacing 2.237 c.c. less than the kilogram of the archives of France. Alloys containing more than 20 per cent. of iridium are very difficult to work.

On the preparation of an ingot of iridio-platinum weighing 250 kilograms, see Morin (*Compt. rend.* lxxviii. 1502; *Jahresb. f. Chem.* 1874, 1065).

On the preparation of pure platinum and pure iridium, see also Deville a. Debray (*Compt. rend.* lxxxi. 839; *Chem. Soc. J.* xxix. 523). The same paper contains the following data of the specific gravities of iridium-platinum alloys.

Platinum	Iridium	Sp. gr.
90	10	21.615
85	15	21.618
66.67	33.3	21.874
5	95	22.384

Sp. gr. of the platinum 21.504 (uncorrected); of the iridium, 22.421.

Expansion by Heat.—The following values of the expansion-coefficient of an alloy of 90 pts. platinum and 10 iridium are given by Fizeau (*Compt. rend.* lxxviii. 1205).

Before pressing	0.000008864
After pressure under the die	9020
After one ignition at 1300°	8905
After two ignitions	8896

According to Deville a. Debray (*N. Arch. ph. nat.* xlvi. 45) an alloy of 90 per cent. platinum and 10 iridium has the same expansion-coefficient as the original meter

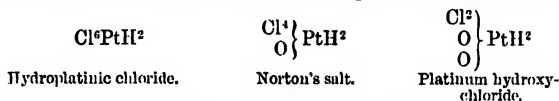
preserved in the French Archives, which is known to have been made with impure platinum.

Chlorides. When platinum is heated to 1400° in a current of an indifferent gas, it neither melts nor volatilises, but if a few bubbles of chlorine are added to the gas, crystals of metallic platinum are deposited on the colder part of the tube. This result is due to the formation, at a very high temperature, of a chloride of platinum which is subsequently decomposed on cooling; if a stream of cold water be passed through a glass tube placed in the axis of the red-hot tube, platinum dichloride will be deposited upon its surface (Troost a. Hautefeuille, *Compt. rend.* lxxxiv. 916).

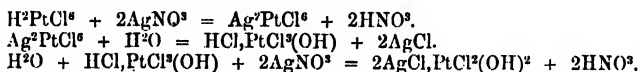
Platinic Chloride, PtCl_4 .—S. M. Jörgensen (*J. pr. Chem.* [2], xvi. 345) finds, in accordance with Weber a. Topsoé (vi. 951), that the compound obtained by evaporating a solution of platinic chloride and drying the residue as completely as possible, consists of hydroplatinic chloride, $\text{PtCl}_4 \cdot 2\text{HCl} + 6\text{H}_2\text{O}$, and not of a hydrate of platinum tetrachloride, $\text{PtCl}_4 + 10\text{H}_2\text{O}$ [or $8\text{H}_2\text{O}$] as supposed by Büdecker, Mathers and Protopopow (vii. 984).

Action of Silver Nitrate.—The addition of silver nitrate in excess to a cold solution of hydroplatinic chloride, throws down the whole of the platinum in the form of a yellow precipitate, having the composition $2\text{AgCl} \cdot \text{PtCl}_4$. This substance has not been obtained in the pure state, as it is slowly decomposed by cold, and rapidly by hot water, into a solution of Norton's salt, $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$ (*J. pr. Chem.* [2], ii. 469; v. 365), and an insoluble residue, consisting of impure silver chloride.

Norton's salt loses 4 mols. of water at 100° ; the fifth molecule cannot be expelled without decomposing the compound. The aqueous solution of this substance has an acid reaction, decomposes carbonates, and produces with silver nitrate a yellow precipitate of the salt $2\text{AgCl} \cdot \text{PtCl}_2(\text{OH})_2$. With ammonia, it forms a precipitate of ammonio-platinic chloride, and the filtrate yields on evaporation a black, amorphous, hygroscopic residue of platinum hydroxychloride. The relation between these bodies is shown by the following formulæ, in which the platinum is octavalent:



The action of silver nitrate on a hot solution of hydroplatinic chloride may be represented by the following equations:

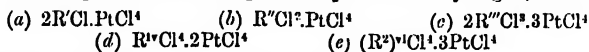


The silver salt obtained by adding silver nitrate to Norton's salt is not analogous to the acid from which it is derived, since it yields by double decomposition with ammonium chloride, platinosemidiammonium chloride, $\text{Cl}^2\text{Pt}^{\text{(N}^2\text{H}^1\text{Cl})}$, and silver chloride (Jörgensen, *loc. cit.*)

Reaction with Stannous Chloride.—When a solution of platinic chloride is mixed with stannous chloride, then largely diluted with water, and heated to boiling, a brown precipitate is formed, analogous to Purple of Cassius. The same precipitate is formed on immersing a plate of tin in the solution of platinic chloride. Its composition, as determined by two analyses, is as follows:

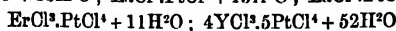
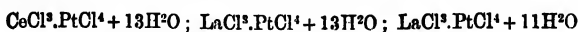
Sn	Pt	O
60.00	11.49	28.51
55.50	17.19	27.31

Chloroplatinates or Platinochlorides (Nilson, *Ber.* ix. 1056, 1142). The formulæ of normal salts of this group may all be derived from that of hydroplatinic chloride, PtCl_4H^2 or $\text{PtCl}_4 \cdot 2\text{HCl}$, or multiples thereof, by substitution of positive metals of various quantivalence for equivalent quantities of hydrogen; thus:



Of these salts all belonging to the formulæ *a* and *b* are known except the mercuric salt (HgCl^2 does not unite with platinic chloride). The beryllium salt, which, according to Thomsen (*Ber.* iii. 827), Marignac (*ibid.* vii. 542), and Welkow (*ibid.* vii. 75), has the composition $\text{BeCl}^2 \cdot \text{PtCl}_4 + 8\text{H}_2\text{O}$, must also be referred to this group, beryllium being regarded as bivalent. The metals of higher quantivalence appear to yield only basic chloroplatinates. Of the decidedly trivalent metals, bismuth, arsenic, and

antimony, no chloroplatinates are known. The chloroplatinates of the cerium and yttrium metals are represented, according to Cleve (pp. 421, 422, 424, 736), by the following formulæ:



According to Frerichs & Smith (pp. 643, 1163), the lanthanum and didymium salts are represented by the formula $2\text{RCl}^3.3\text{PtCl}^4 + 24\text{H}^2\text{O}$.

Of the chloroplatinates of metals with combined quadrivalent atoms, only the *aluminium salt*, $\text{Al}^2\text{Cl}^6.2\text{PtCl}^4 + 30\text{H}^2\text{O}$, analysed by Welkow (p. 65), has hitherto been known. The following have been obtained by Nilson from mixtures of 1 mol. of the chloride R^2Cl^6 , with 2 mol. platonic chloride.

$\text{Fe}^2\text{Cl}^6.2\text{PtCl}^4 + 21\text{H}^2\text{O}$. Large, yellow, well-defined, oblique, four-sided, deliquescent prisms, which give off $10\text{H}^2\text{O}$ at 100° .

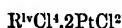
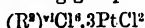
$\text{Cr}^2\text{Cl}^6.2\text{PtCl}^4 + 21\text{H}^2\text{O}$. Fine, green, four-sided, deliquescent prisms, which give off $10\text{H}^2\text{O}$ at 100° .

$\text{In}^2\text{Cl}^6.5\text{PtCl}^4 + 36\text{H}^2\text{O}$. Honey-yellow, oblique, four-sided prisms, with oblique end-faces, deliquescent on exposure to the air, and giving off half their water at 100° .

The ferric and chromic salts are, therefore, analogous to the aluminium salt, as are also those of the cerium and yttrium metals, if the formulæ of these salts are doubled, and they are supposed to crystallise with quantities of water, which, according to Nilson, are more in accordance with the analyses than those which are assigned to the respective salts by Cleve.

Of the chloroplatinates of quadrivalent metals, only the *thorium salt*, $\text{ThCl}^4.\text{PtCl}^4 + 12\text{H}^2\text{O}$, analysed by Cleve, has hitherto been known. Nilson has also prepared the *tin* and *zirconium salts*, and found them to be analogous in composition to the thorium salt. The *tin salt*, $\text{SnCl}^4.\text{PtCl}^4 + 12\text{H}^2\text{O}$, crystallises in small, shining, light-green, thin, four-sided, perhaps somewhat oblique plates. *Zirconium oxychloroplatinate*, $\text{ZrOCl}^2.\text{PtCl}^4 + 12\text{H}^2\text{O}$, forms small, honey-yellow, oblique, four-sided plates.

Chloroplatinites or Platinosochlorides (Nilson, *J. pr. Chem.* [2], xv. 260). These salts may be arranged in the four following groups:



Most of those here described were prepared by decomposing barium chloroplatinite with the respective sulphates; in some cases, however, by saturating the free acid, $2\text{HCl}.\text{PtCl}^2$, with oxides, hydroxides, carbonates, or chlorides.

The chloroplatinites are usually very soluble in water; they are for the most part deliquescent, and crystallise only from very concentrated solutions; most of them contain water of crystallisation. At 100° they are decomposed, with production of metallic platinum, a few evolving hydrochloric acid. By evaporating their solutions in presence of hydrochloric acid, the platinum is usually partially converted into platonic chloride. The following new chloroplatinites have been obtained:

$2\text{RbCl}.\text{PtCl}^2$. Small, four-sided, red prisms, unaltered in air, easily soluble in hot water, sparingly soluble in cold water.

$2\text{CsCl}.\text{PtCl}^2$. Long slender prisms, resembling the rubidium salt.

$2\text{TlCl}.\text{PtCl}^2$. Prisms of a light-pink colour, difficultly soluble in hot water.

$2\text{LiCl}.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Dark-red four-sided prisms, with greenish lustre, resembling potassium permanganate; easily soluble in water.

$\text{CaCl}^2.\text{PtCl}^2 + 8\text{H}^2\text{O}$. Thin, flexible tables; over sulphuric acid it assumes a rose colour; melts at 100° , giving up 5 mols. of water, and then decomposing into chloroplatinate and platinum: very deliquescent.

$\text{SrCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Resembles the calcium salt: gives up two-thirds of its water at 100° .

$\text{PbCl}^2.\text{PtCl}^2 + 5\text{H}^2\text{O}$. Amorphous red powder; decomposed slowly by boiling water.

$\text{BeCl}^2.\text{PtCl}^2 + 5\text{H}^2\text{O}$. Red rhombohedrons: deliquesces in moist air: unchanged in dry air; gives up water and HCl at 100° . Easily soluble in water.

$\text{MgCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Tables, unaltered in air; give up no crystalline water at 100° .

$\text{MnCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Resembles the preceding: gives up two-thirds of its water at 100° .

$\text{CoCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Red four- or six-sided tables: gives up 5 mols. H^2O at 100° .

$\text{NiCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Dark-brown tables: gives up 3 mols. H^2O at 100° .

$\text{CuCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Olive-brown or nearly black tables: gives up 5 mols. H^2O at 100° .

$\text{ZnCl}^2.\text{PtCl}^2 + 6\text{H}^2\text{O}$. Tables: gives up 6 mols. H^2O at 100° , decomposing also into chloroplatinate and platinum.

$\text{FeCl}^2.\text{PtCl}^2 + 7\text{H}^2\text{O}$. Dark-red prisms: gives up 5 mols. H^2O at 100° .

Cadmium chloroplatinite could not be obtained.

$\text{Al}^3\text{Cl}^4.2\text{PtCl}^2 + 21\text{H}^2\text{O}$. Large brilliant four-sided prisms: melts at 100° , and gives up 19 mols. H^2O .

$\text{Cr}^3\text{Cl}^4.3\text{PtCl}^2 + 18\text{H}^2\text{O}$. Thin, red, deliquescent prisms, giving up water and hydrochloric acid at 100° .

$\text{Y}^2\text{Cl}^4.3\text{PtCl}^2 + 24\text{H}^2\text{O}$. Dark-red, four-sided prisms: melts at 100° , and gives up 10 mols. H^2O .

$\text{Er}^2\text{Cl}^4.2\text{PtCl}^2 + 27\text{H}^2\text{O}$. Dark-red prisms: at 100° gives up 17 mols. H^2O .

$\text{Er}^2\text{Cl}^4.3\text{PtCl}^2 + 24\text{H}^2\text{O}$. Long four-sided prisms: loses 11 mols H^2O at 100° .

$\text{Ce}^2\text{Cl}^4.4\text{PtCl}^2 + 21\text{H}^2\text{O}$. Thin four-sided prisms: loses 15 mols. H^2O at 100° .

$\text{La}^2\text{Cl}^4.3\text{PtCl}^2 + 18\text{H}^2\text{O}$. Like the last.

$\text{La}^2\text{Cl}^4.3\text{PtCl}^2 + 27\text{H}^2\text{O}$. Prisms: gives up 16 mols. H^2O at 100° .

$\text{Di}^2\text{Cl}^4.4\text{PtCl}^2 + 21\text{H}^2\text{O}$. Prisms or tables: deliquescent in air.

$\text{Di}^2\text{Cl}^4.3\text{PtCl}^2 + 18\text{H}^2\text{O}$. Long thin prisms.

$2\text{ThCl}^4.3\text{PtCl}^2 + 24\text{H}^2\text{O}$. Rhombohedrons: gives up one-fourth of its water at 100° without melting.

$\text{ZrOCl}^2.\text{PtCl}^2 + 8\text{H}^2\text{O}$. Large quadratic prisms.

$2\text{HCl}.\text{PtCl}^2 + x\text{H}^2\text{O}$. Produced by decomposing the barium salt with the equivalent quantity of sulphuric acid, and evaporating in a vacuum. The solution, after reaching a certain degree of concentration, evolves hydrochloric acid, leaving a dark-brown amorphous mass, easily soluble in water, giving up water and hydrochloric acid at 100° .

J. Thomsen (*J. pr. Chem.* [2], xv. 204) prepares *potassium chloroplatinite* from the chloroplatinate by reduction with cuprous chloride. The moist chloroplatinate is mixed with water to a pasty consistence, the mass is warmed, and moist cuprous chloride is cautiously added in such quantity as to leave a small portion of the potassium chloroplatinate undissolved. A nearly black solution is thereby formed, from which, after filtration and cooling, the chloroplatinite is deposited in fine red crystals, which may be purified by washing with alcohol. *Hydrogen chloroplatinite*, PtCl^4H^2 , is easily obtained by mixing a concentrated solution of the potassium salt with platinic chloride. Potassium chloroplatinate then separates out, and the red solution contains the hydrogen chloroplatinite, which may be used immediately to prepare the other chloroplatinites. The *ammonium salt*, $\text{PtCl}^4(\text{NH}^4)^2$, easily obtained by mixing the solution of the hydrogen salt with ammonium chloride and evaporating, crystallises in large red needles.

Potassium Bromoplatinite, PtBr^4K^2 , is formed when potassium chloroplatinite and sodium bromide are boiled together with so small a quantity of water that the greater part of the resulting sodium chloride separates out. On leaving the hot filtrate to cool, the bromoplatinite separates in large nearly black rhombic octohedrons, or, if quickly cooled, in brown-red very soluble needles.

Sodium bromoplatinate, PtBr^4Na^2 , is most readily obtained by heating a concentrated solution of platinic chloride with hydrobromic acid, driving off the resulting hydrochloric acid by evaporation, then adding sodium bromide, evaporating to dryness, and purifying the saline mass by recrystallisation (Thomsen).

On *Cyanides of Platinum*, see p. 616. On *Ammonio-platinic and Potassio-platinic Thiocyanate*, see p. 603.

Platinous Hydroxide, $\text{Pt}(\text{OH})^2$, is formed as a black precipitate on boiling a very dilute solution of potassium chloroplatinite with a sufficient quantity of dilute soda-ley. It dissolves readily at a gentle heat in dilute hydrochloric or hydrobromic acid; and is reduced by dilute formic acid, with evolution of carbon dioxide, to metallic platinum (Thomsen, *J. pr. Chem.* [2], xvi. 294).

Platinoso-platinic Oxide, Pt^2O^4 , is prepared by heating dehydrated sodium chloroplatinate with sodium carbonate till the mass begins to melt, and boiling the melt with water and dilute nitric acid. When dried at 100° it is blue-black in lumps, pure black in powder; it is not attacked by hydrochloric, nitric, or nitrohydrochloric acid, even after prolonged boiling. It slowly gives off its oxygen at a red heat. Hydrogen and coal-gas, even at ordinary temperatures, reduce it, with vivid ignition and formation of water. Formic acid at a gentle heat reduces it, with evolution of carbon dioxide, to platinum black (Jørgensen, *J. pr. Chem.* [2], xvi. 344).

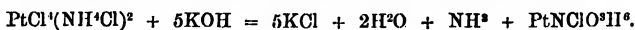
NITROGEN-COMPOUNDS OF PLATINUM.

Platinosemiammonium Chloride, $\text{Cl}^2\text{Pt} \begin{smallmatrix} \text{N}^2\text{H}^4\text{Cl} \\ \text{Cl} \end{smallmatrix}$.—This compound, which Cleve obtained by the action of chlorine on platosemiammonium chloride, $\text{Cl}.\text{Pt}.\text{N}^2\text{H}^4\text{Cl}$ (vii. 997), is also formed by the action of a cold strong solution of ammonium chloride

on the salt $\text{Cl}^1\text{O}\}\text{PtH}^3$ (p. 1648). The corresponding *iodide*, $\text{PtI}^1\text{N}^3\text{H}^6$, formed by treating the chloride with potassium iodide, separates from a solution containing ammonium chloride in small shining crystals resembling iodine, appearing under the microscope as multiform groups of apparently regular six-sided plates; from aqueous solution it separates in powdery crystals having an iodine-grey colour, and appearing under the microscope as rectangular prisms bevelled by a dome (Jørgensen, *J. pr. Chem.* [2], xvi. 345).

Fulmiplatinums (E. v. Meyer, *J. pr. Chem.* [2], xviii. 324). *Knallplatine*.—These are compounds obtained by the action of potash on ammonium chloroplatinate, $\text{PtCl}^1(\text{NH}^1\text{Cl})^2$. They are nearly insoluble in water, and do not form definite compounds with either acids or alkalis. The nitrogen contained in them is so firmly held in combination that they give off no ammonia when boiled with strong potash solution. When heated *per se* they undergo total decomposition, generally with explosive violence, owing to the sudden liberation of a large quantity of nitrogen.

When ammonium chloroplatinate is boiled with a quantity of aqueous potash insufficient for complete decomposition, added very slowly, a product of the formula $\text{PtNClO}^3\text{H}^6$ is obtained, the formation of which may be represented thus:



The chemical behaviour of this body, and the existence of other bodies standing in simple relation to it, show, however, that the foregoing formula must be quadrupled, making it $\text{Pt}^4\text{N}^4\text{Cl}^4\text{O}^{12}\text{H}^{24}$ (*tetrachlorofulmiplatinum*). Its relations to the other fulmiplatinums may then be exhibited by the following equations, which indicate the derivation from it of (1) *trichlorohydroxyfulmiplatinum*, (2) *dichlorofulmiplatinum*, and (3) *chlorhydroxyfulmiplatinum*:

- (1). $\text{Pt}^4\text{N}^4\text{Cl}^4\text{O}^{12}\text{H}^{24} + 4\text{KOH} = 4\text{KCl} + \text{Pt}^4\text{N}^4\text{Cl}^1(\text{OH})\text{O}^{11}\text{H}^{24}$
- (2). $\text{Pt}^4\text{N}^4\text{Cl}^4\text{O}^{12}\text{H}^{24} + 2\text{KOH} = 2\text{KCl} + \text{Pt}^4\text{N}^4\text{Cl}^2\text{O}^{12}\text{H}^{22} + 2\text{H}^2\text{O}$
- (3). $\text{Pt}^4\text{N}^4\text{Cl}^4\text{O}^{12}\text{H}^{24} + 3\text{KOH} = 3\text{KCl} + \text{Pt}^4\text{N}^4\text{Cl}^1(\text{OH})\text{O}^{11}\text{H}^{22} + 2\text{H}^2\text{O}$

The constitution of these bodies is as yet undetermined.

Tetrachlorofulmiplatinum, $\text{Pt}^4\text{N}^4\text{Cl}^4\text{O}^{12}\text{H}^{24}$.—The preparation of this compound in the pure state is attended with great difficulty, one of its atoms of chlorine being very easily eliminated. It is formed on heating ammonium chloroplatinate with aqueous potash (4.6 mols.), added very slowly until a temporary alkaline reaction is produced. The pale yellow precipitate is purified by repeated boiling with very dilute acetic acid and water. A slight excess of potash determines the formation of bodies containing less chlorine.

It gives up half its chlorine when digested with aqueous ammonia, and three-fourths when evaporated with ammonia over the water-bath: whence it appears that two atoms of chlorine are eliminated easily, and a third less easily, whilst the first is firmly held in combination. The bodies formed from it by the action of ammonia explode violently when heated; they have not been fully investigated. When gently heated with oxalic acid in presence of dilute sulphuric acid, tetrachlorofulmiplatinum gives off a quantity of carbon dioxide corresponding to a loss of 3 atoms of oxygen from each mol. At 150° it gives off 4 mols. of water.

Trichlorofulmiplatinum, $\text{Pt}^4\text{N}^4\text{Cl}^3(\text{OH})\text{O}^{11}\text{H}^{24}$, is formed when ammonium chloroplatinate is decomposed with an insufficient quantity of potash (4.5–5 mols.), added in small portions somewhat rapidly. At 150° , it loses 3 mols. of water, and when more strongly heated, it explodes, giving off gases which consist mainly of nitrogen, but contain also free oxygen. When treated with ammonia, it gives up 2 atoms of chlorine. It is acted on by oxalic acid in the same manner as the previous compound, the carbon dioxide evolved corresponding with the loss of 3 atoms of oxygen from each molecule. After the reaction the liquid contains a black precipitate, which gives off ammonia when heated with soda. When gently heated in hydrogen, the trichloro-compound undergoes violent decomposition, yielding water, ammonia, and free nitrogen.

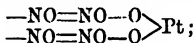
Dichlorofulmiplatinum, $\text{Pt}^4\text{N}^4\text{Cl}^2\text{O}^{12}\text{H}^{22}$, is formed on heating ammonium chloroplatinate with aqueous potash, added in moderate quantities until the liquid remains slightly alkaline and ceases to evolve ammonia. It is a fine yellow body, closely resembling the compound last described in most of its reactions. It is completely decomposed by treatment with zinc and sulphuric acid, the platinum being thrown down in a finely divided metallic state, whilst the whole of the chlorine goes into solution. Sulphur dioxide passed into water in which the compound is suspended, gradually dissolves it, forming a nearly colourless solution, which when neutralised

with sodium carbonate and evaporated, yields crystals of Birnbaum's salt, $(\text{PtSO}_3 \cdot 3\text{Na}_2\text{SO}_3) \cdot 3\text{H}_2\text{O}$ (*Liebig's Annalen*, cxxxix. 169).

Chlorohydroxyfulmiplatinum, $\text{Pt}^{\text{IV}}\text{Cl}(\text{OH})\text{O}^{12}\text{H}^{22}$, is obtained as a dark yellow powder by heating ammonium chloroplatinate with 4.7 mols. of aqueous potash added at once, until ammonia is no longer evolved. It loses 4 mols. of water at 152° . When it is gradually heated to 260° with sodium carbonate, nearly the whole of the hydrogen is oxidised to water, whilst the hydrogen is for the most part set free. It is not appreciably acted upon by oxalic acid. With nascent hydrogen, it behaves like the dichloro-compound.

The foregoing results show that the decomposition of ammonium chloroplatinate by potash results in the formation of bodies containing equal numbers of atoms of platinum and nitrogen, whence it follows that ammonium chloroplatinate cannot be regarded as a double salt of platonic chloride and ammonium chloride, $\text{PtCl}_4(\text{NH}_4\text{Cl})_2$, the 2 atoms of nitrogen having essentially different functions in the compound. Direct experiment shows that when ammonium chloroplatinate is heated even with a large excess of potash, only half the nitrogen is eliminated in the form of ammonia.

Platonitrites and Diplatonitrites (Nilson, *J. pr. Chem.* [2], xvi. 241-278). Lang in 1861 discovered a double salt of platinum, which was produced on heating mixed solutions of potassium chloroplatinate and potassium nitrite (iv. 672). The composition of the salt was found to agree with the formula $\text{K}^2\text{Pt}(\text{NO}_2)_4$, but its constitution was not then understood. Blomstrand in 1871 (*J. pr. Chem.* [2], iii. 186) assigned to the salt, on theoretical grounds, the formula $(\text{K}-\text{O}-\text{NO}=\text{NO}-\text{O})^2\text{Pt}$, in which the platinum was supposed to play the part of a diatomic element; and this formula was supported by the fact, discovered by Blomstrand, that the salt readily takes up 2 atoms of chlorine or bromine to form a compound of tetratomic platinum. On this view the salt may be regarded as containing the negative radicle *platotetra-nitrosyl*:



and accordingly the corresponding acid (Lang's acid *platinous nitrite*) may be called *Platotetranitrous*, *Platinotetranitrosylic*, or simply *Platonitrous acid*, and its salts *Platonitrites*.

The following platonitrites have been prepared and analysed by Nilson. Except where otherwise stated, they were obtained by decomposing barium platonitrite with the sulphates of the respective bases.

The *potassium salt*, $\text{K}^2(\text{NO}_2)_4\text{Pt}$, crystallises from mixed solutions of potassium platinochloride and potassium nitrite in small colourless brilliant four- or six-sided prisms; it crystallises without water from a solution of potassium chloride, but with 2 mols. of water from aqueous solution.

The *rubidium and caesium salts*, $\text{Rb}^2(\text{NO}_2)_4\text{Pt}$ and $\text{Cs}^2(\text{NO}_2)_4\text{Pt}$, obtained by decomposing silver platonitrite with rubidium or caesium chloride, crystallise in small colourless or faintly-yellow transparent needles, which are permanent in the air and at 100° , and dissolve sparingly in water. The rubidium salt separates from a dilute solution on spontaneous evaporation in crystals containing 2 mols. of water.

Ammonium salt, $(\text{NH}_4)^2(\text{NO}_2)_4\text{Pt} + 2\text{H}_2\text{O}$.—Formed by triturating equivalent proportions of silver platonitrite and ammonium chloride with a little water. Crystallises in brilliant colourless or yellowish six-sided rhombic prisms, which are permanent in the air, but lose their water over sulphuric acid. The salt is decomposed with explosive violence when heated in the slightest degree over an open flame, leaving a bulky residue of spongy platinum.

Thallium salt, $\text{Tl}^2(\text{NO}_2)_4\text{Pt}$.—Crystallises in small brilliant, colourless, semi-transparent prisms, very sparingly soluble in cold water, and stable in the air and at 100° .

Sodium salt, $\text{Na}^2(\text{NO}_2)_4\text{Pt}$.—From the silver salt and sodium chloride. Crystallises in long colourless six-sided rhombic prisms, easily soluble in water, and permanent at 100° .

Lithium salt, $\text{Li}^2(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Obtained as the last. Crystallises in beautiful short rhombic prisms, which dissolve easily in water, turn moist in the air, and give off their water of crystallisation at 100° .

Silver salt, $\text{Ag}^2(\text{NO}_2)_4\text{Pt}$.—Obtained by decomposing potassium platonitrite with silver nitrate, and crystallising the product repeatedly in presence of excess of silver nitrate. Small yellowish monoclinic four-sided prisms, permanent in the air, and sparingly soluble in cold water.

Calcium salt, $\text{Ca}(\text{NO}_2)_4\text{Pt} + 5\text{H}_2\text{O}$.—Obtained by double decomposition of the

silver salt and calcium chloride. Forms thin yellowish oblique four-sided prisms, which are permanent in moist air, but effloresce over sulphuric acid, and lose the whole of their water at 100° . The salt is very easily soluble.

Strontium salt, $\text{Sr}(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Obtained as the last. Forms large colourless or yellowish six-sided prisms, which dissolve easily in water, lose two-thirds of their water at 100° , and bear a high temperature without decomposition.

Barium salt, $\text{Ba}(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Obtained as the calcium salt. Crystallises very readily in colourless brilliant tables or prisms, sparingly soluble in cold water, and permanent in the air.

Lead salt, $\text{Pb}(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Obtained as the calcium salt. Crystallises over sulphuric acid in yellow opaque six-sided monoclinic prisms, which lose their water at 100° .

Magnesium salt, $\text{Mg}(\text{NO}_2)_4\text{Pt} + 5\text{H}_2\text{O}$.—Colourless transparent six-sided monoclinic prisms, easily soluble in water, permanent in the air and at 100° , but decomposed with great tumefaction by gentle heating.

Manganese salt, $\text{Mn}(\text{NO}_2)_4\text{Pt} + 8\text{H}_2\text{O}$.—Crystallises in beautiful large rose-red triclinic prisms, which gradually turn darker in the air. Blackens at 100° , evolving nitric oxide.

Cobalt salt, $\text{Co}(\text{NO}_2)_4\text{Pt} + 8\text{H}_2\text{O}$.—Large red prisms, isomorphous with the last. Easily soluble in water; permanent in the air; decomposed at 100° .

Nickel salt, $\text{Ni}(\text{NO}_2)_4\text{Pt} + 8\text{H}_2\text{O}$.—Beautiful green transparent very thin tables or laminae, which are easily soluble in water and permanent in the air, but decomposed at 100° , giving off red vapours.

Copper salt (basic), $[\text{Cu}(\text{NO}_2)_4\text{Pt}]_3\text{CuO} + 18\text{H}_2\text{O}$.—From the barium salt and cupric sulphate. Crystallises in golden-yellow delicate needles, which are decomposed by water, giving a green solution and a dark-coloured precipitate.

Copper salt (normal), $\text{Cu}(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Crystallises from the mother-liquor of the preceding salt in very small green needles, which dissolve easily in water. Decomposed at 100° .

Zinc salt, $\text{Zn}(\text{NO}_2)_4\text{Pt} + 8\text{H}_2\text{O}$.—Large colourless or yellowish transparent crystals, isomorphous with those of the manganese, cobalt, and nickel salts. Easily soluble in water. Decomposed at 100° .

Cadmium salt, $\text{Cd}(\text{NO}_2)_4\text{Pt} + 3\text{H}_2\text{O}$.—Large yellow transparent monoclinic prisms, easily soluble in water, and efflorescent in the air. Gives off its water at 100° without further decomposition.

Mercurous salt, $\text{Hg}_2(\text{NO}_2)_4\text{Pt} \cdot \text{Hg}_2\text{O} + \text{H}_2\text{O}$.—Precipitated on mixing solutions of potassium platinitrite and mercurous nitrate. Small pointed prisms nearly insoluble in water, and becoming anhydrous at 60° .

Aluminium salt, $\text{Al}_2[(\text{NO}_2)_4\text{Pt}]_3 + 14\text{H}_2\text{O}$.—Large colourless apparently cubical crystals, very easily turning red owing to formation of diplatonitrite (see below). Decomposed at 100° .

Yttrium salt, $\text{Y}_2[(\text{NO}_2)_4\text{Pt}]_3 + 9\text{H}_2\text{O}$.—Small lemon-yellow, oblique four-sided prisms, permanent in the air and easily soluble in water. The mother-liquor deposits a salt with 21 mols. water, in long colourless or yellowish crystals, which lose 18 mols. of water at 100° .

Erbium salt, $\text{Er}_2[(\text{NO}_2)_4\text{Pt}]_3 + 9\frac{1}{2}\text{H}_2\text{O}$.—Small yellow oblique four-sided prisms, easily soluble in water and permanent in the air. Another salt containing 21 mols. water is deposited from the mother-liquor in large reddish crystals.

Cerium salt, $\text{Ce}_2[(\text{NO}_2)_4\text{Pt}]_3 + 18\text{H}_2\text{O}$.—Yellowish oblique four-sided tables or rhombohedrons, easily soluble in water. The salt quickly undergoes alteration in the air and loses 15 mols. water at 100° .

Lanthanum salt, $\text{La}_2[(\text{NO}_2)_4\text{Pt}]_3 + 18\text{H}_2\text{O}$.—Closely resembles the preceding. Dissolves very easily in water, and deliquesces in moist air.

Didymium salt, $\text{Di}_2[(\text{NO}_2)_4\text{Pt}]_3 + 18\text{H}_2\text{O}$.—Resembles the two last. Easily soluble in water; permanent in dry air; loses five-sixths of its water at 100° .

Plato-iodonitrites, $\text{R}^2\text{N}^2\text{O}^4\text{I}^2\text{Pt} = \text{R}^2(\text{NO}_2)_2\text{I}^2\text{Pt}$ (Nilson, *Ber.* x. 930; xi. 879). These salts are formed by the action of iodine and alcohol on the platonitrites. When 1 mol. iodine in alcoholic solution is brought in contact with 1 mol. platonitrite of potassium or barium, a dark brown-red liquid is formed, which, when left to evaporate, deposits small black crystals, probably of an addition-product; but on heating the liquid to 30° – 40° , it rapidly gives off gas, including aldehyde-vapour, becomes lighter in colour and finally amber-yellow, and when left to evaporate yields crystals of the plato-iodonitrite. The *potassium salt*, $\text{K}^2\text{N}^2\text{O}^4\text{I}^2\text{Pt} + 2\text{H}_2\text{O}$, crystallises in large four-

sided, shining, amber-yellow prisms, which are permanent in the air, and give off nothing but their water of crystallisation at 100° . The platinum in this salt is not precipitated by hydrogen sulphide, or the iodine by silver nitrate. The *barium salt*, $\text{BaN}^{\circ}\text{O}^{\text{I}}\text{Pt} + 4\text{H}^{\circ}\text{O}$, crystallises in beautiful oblique four-sided prisms having an amber-yellow colour and diamond lustre, permanent in the air, and giving off part of their water at 100° . The *silver salt* is thrown down on adding silver nitrate to the solution of either of the preceding salts, as a lemon-yellow precipitate which is very slightly soluble in water, and when left upon filter-paper, acquires a blood-red colour, being probably resolved into silver iodide and a platinonitrosylic acid.

The other plato-iodonitrites are mostly prepared by the action of a metallic sulphate on barium platoiodonitrite. The silver, lead, and hydrogen-compounds are, however, precipitated from the barium salt by their respective nitrates, and the calcium and strontium platoiodonitrites are obtained from the platonitrites by the action of iodine and alcohol. The silver, lead, thallium, and hydrogen salts are insoluble in water, the remaining salts are soluble. Most of the platoiodonitrites are very stable, and do not decompose at 100° ; others, however, split up into nitrite and platinum iodide.

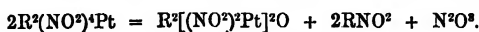
Rubidium platoiodonitrite, $\text{Rb}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 2\text{H}^{\circ}\text{O}$, forms large shining tabular crystals, which lose their water of crystallisation at 100° . The *cæsium salt*, $\text{Cs}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 2\text{H}^{\circ}\text{O}$, crystallises in small prisms, which lose their 2 mols. of water at 100° . The *ammonium salt*, $(\text{NH}^{\text{I}})^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 2\text{H}^{\circ}\text{O}$, forms large tabular crystals, which decompose slowly at 70° , but rapidly at 100° into water, nitrogen, and platinum iodide. *Thallium platoiodonitrite*, $\text{Tl}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt}$, separates out as an insoluble crystalline precipitate, when sodium platoiodonitrite is added to a solution of thallium sulphate. The *sodium salt*, $\text{Na}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 4\text{H}^{\circ}\text{O}$, crystallises in large prisms, which lose their water at 100° . The *lithium salt*, $\text{Li}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 6\text{H}^{\circ}\text{O}$, forms long deliquescent prisms, which lose 5 mols. water at 100° . The *calcium salt*, $\text{Ca}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 6\text{H}^{\circ}\text{O}$, crystallises in large prisms, which only lose 1 mol. water at 100° . The *strontium salt*, $\text{Sr}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 8\text{H}^{\circ}\text{O}$, forms large four-sided prisms which give off 6 mols. water at 100° . The *lead salt*, $\text{Pb}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + \text{PbO}^{\circ}\text{H}^{\circ}$, is precipitated on the addition of lead nitrate to the barium salt. The *magnesium salt*, $\text{Mg}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 8\text{H}^{\circ}\text{O}$, crystallises in large four-sided tables; the *manganese salt*, $\text{Mn}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 8\text{H}^{\circ}\text{O}$, is deposited in irregular six-sided prisms, which are completely decomposed at 100° . *Nickel and cobalt platoiodonitrites* form respectively green and yellow four-sided prisms, containing 8 mols. water, and decomposing at 100° . The *ferrous salt* crystallises in greenish-yellow four-sided prisms, containing 8 mols. water, and is decomposed at 100° . The *copper salt* has not been obtained in the pure state. *Zinc platoiodonitrite*, $\text{Zn}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 8\text{H}^{\circ}\text{O}$, forms four-sided prisms, which are decomposed at 100° . The *cadmium-compound*, $\text{Cd}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + 2\text{H}^{\circ}\text{O}$, does not change when heated at 100° .

When mercuric chloride is added to barium platoiodonitrite, mercuric iodide is precipitated; mercurous nitrate produces a dark-brown precipitate having the formula $\text{Hg}^{\circ}\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt} + \text{Hg}^{\circ}\text{O} + 9\text{H}^{\circ}\text{O}$.

Beryllium platoiodonitrite, $\text{Be}^{\circ}(\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt})^3 + 18\text{H}^{\circ}\text{O}$, [$\text{Be} = 13.8$], or $\text{BeN}^{\circ}\text{O}^{\text{I}}\text{Pt} + 6\text{H}^{\circ}\text{O}$ [$\text{Be} = 9.2$], forms small yellow crystals, which decompose at 100° . The aluminium salt contains 27 mols. of water, and in other respects resembles the preceding compound. The solution of the *chromium salt* decomposes on evaporation in a vacuum. *Ferric platoiodonitrite*, $\text{Fe}^{\circ}(\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt})^3 + 6\text{H}^{\circ}\text{O}$, crystallises in greenish-yellow needles, which decompose at 100° .

Yttrium platoiodonitrite, $\text{Y}^{\circ}(\text{N}^{\circ}\text{O}^{\text{I}}\text{Pt})^3 + 27\text{H}^{\circ}\text{O}$, is a yellowish-green deliquescent crystalline mass, which decomposes at 100° . The erbium and cerium salts contain 18 mols. of water, lanthanum and didymium contain 24; in other respects these platoiodonitrites resemble the yttrium-compound.

Diplatonitrites, $\text{R}^{\circ}[(\text{NO}^{\circ})^2\text{Pt}]^2\text{O}$, or $\frac{\text{R.O.NO}=\text{NO.O.Pt}}{\text{R.O.NO}=\text{NO.O.Pt}} > \text{O}$, R denoting a univalent metal. On attempting to prepare the platonitrites of beryllium, iron, and indium in the manner above described, it was found that these salts could not be obtained, but that, instead of them, the corresponding diplatonitrites were produced, being formed from the platonitrites, with evolution of nitrogen trioxide, as shown by the equation



Some of the platonitrites above described are also partially converted into diplatonitrites when their solutions are heated. The following diplatonitrites have been analysed:

Beryllium salt, $\text{Be}[(\text{NO}^{\circ})^2\text{Pt}]^2\text{O} + 9\text{H}^{\circ}\text{O}$.—Red prismatic crystals, sparingly soluble in water, forming a bright-yellow solution. Loses two-thirds of its water at 100° .

Ferric salt, $\text{Fe}^2[(\text{NO}^2)^2\text{Pt}]^4\text{O}^3 + 30\text{H}^2\text{O}$.—Resembles the beryllium salt. Easily soluble in hot water. Loses four-fifths of its water at 100° .

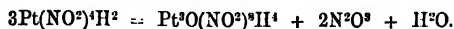
Indium salt, $\text{In}^2(\text{OH})^2[(\text{NO}^2)^2\text{Pt}]^4\text{O}^2 + 10\text{H}^2\text{O}$.—Very small red needles sparingly soluble in water, forming an orange-red solution.

Silver salt, $\text{Ag}^2[(\text{NO}^2)^2\text{Pt}]^4\text{O}$.—Tufts of greenish very small four-sided prisms, insoluble in water.

Aluminium salt, $\text{Al}^2(\text{OH})^2[(\text{NO}^2)^2\text{Pt}]^4\text{O}^2 + 10\text{H}^2\text{O}$.—Brilliant orange-red small needles, permanent in the air, easily soluble in hot water and alcohol.

Chromium salt, $\text{Cr}^2(\text{OH})^2[(\text{NO}^2)^2\text{Pt}]^4\text{O}^2 + 24\text{H}^2\text{O}$.—Small red crystals forming a greenish-violet solution in water. Gives off 18 mols. water at 100° .

Triplutocetonitrosylic acid, $\text{Pt}^2\text{O}(\text{NO}^2)^3\text{H}^4$, is formed, with evolution of nitrogen trioxide, when an aqueous solution of platinonitrous or platinotetranitrosylic acid is left to evaporate:



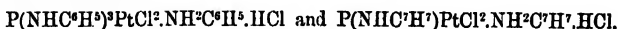
It is permanent at 100° , and forms a potassium salt, $\text{Pt}^2\text{O}(\text{NO}^2)^3\text{K}^4 + 2\text{H}^2\text{O}$, which crystallises in small oblique elongated four-sided plates, having a chrome-yellow colour and nacreous lustre, dissolves with moderate facility in warm water, and crystallises out again immediately on cooling. It is permanent in the air, and gives off nothing but its water of crystallisation at 100° .

PHOSPHOPLATINIC COMPOUNDS.

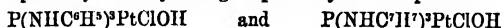
G. Quesneville (*Monit. scient.* [3], vi. 659) has studied the action of ammonia and aromatic amines (aniline, toluidine) on the compounds $\text{Cl}^3\text{P} = \text{PtCl}^2$ and $\begin{array}{c} \text{Cl}^3\text{P} \\ | \\ \text{Cl}^3\text{P} \end{array} \rangle \text{PtCl}^2$, first obtained by Baudrimont, and further examined by Schützenberger (vii. 987, 990).

On adding ammonia to a solution of phosphoplatinic chloride, $\text{PtCl}^2\text{PtCl}^2$, in benzene, a white precipitate is formed, having the composition $\text{P}(\text{NH}^2)^3\text{Pt}^2\text{N}^2\text{H}^4.2\text{HCl} + 3\text{NH}^4\text{Cl}$, but whether the ammonium chloride and the phosphoplatinum compound are chemically combined or merely mixed has not yet been decided, as the two appear to be about equally soluble in water. The *ethyl ether*, $\text{P}(\text{OC}^2\text{H}^3)^3\text{PtCl}^2$, obtained from the chloride by the action of alcohol, is acted on by ammonia in a similar manner, yielding the compound $\text{P}(\text{OC}^2\text{H}^3)^3\text{Pt}^2\text{N}^2\text{H}^4.2\text{HCl}$. The chloride, $(\text{PtCl}^2)^2\text{PtCl}^2$, gives with ammonia the compound $\text{P}^2(\text{NH}^2)^6\text{Pt}^2\text{N}^2\text{H}^4.2\text{HCl} + 6\text{NH}^4\text{Cl}$; and the corresponding ether, $\text{P}^2(\text{OC}^2\text{H}^3)^6\text{PtCl}^2$, yields the compound $\text{P}^2(\text{OC}^2\text{H}^3)^6\text{Pt}^2\text{N}^2\text{H}^4.2\text{HCl}$.

The action of the aromatic amines on the phosphoplatinic chlorides is somewhat different, yielding compounds soluble in benzene, but insoluble in water, and represented by the formulæ:

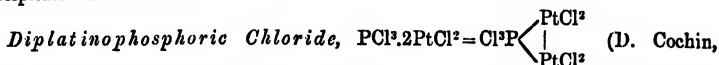


They are decomposed by water, yielding respectively the compounds:



A similar action is exerted by aniline and toluidine on the ethers of phosphoplatinic chloride, the product being the aniline-compound $\text{P}(\text{OC}^2\text{H}^3)^3\text{PtCl}^2.\text{NH}(\text{C}^6\text{H}^5)$, being converted by the action of potassium hydrate into $\text{P}(\text{OC}^2\text{H}^3)^3\text{Pt}(\text{OH})^2.\text{NH}(\text{C}^6\text{H}^5)$.

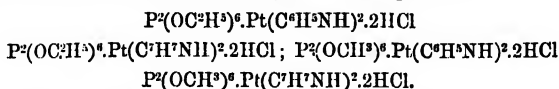
Amongst the products of the action of aniline on diphosphoplatinic chloride, $(\text{PtCl}^2)^2\text{PtCl}^2$, only the compound $\text{P}^2\text{O}(\text{NHC}^2\text{H}^3)^6\text{PtClOH}$ could be obtained pure; it is formed when the alcoholic solution of the immediate product of the reaction is precipitated with water.



Compt. rend. lxxxvi. 1402).—This compound is formed by fusing phosphoplatinic chloride with platinous chloride. A considerable rise of temperature takes place, and the mass thickens, becoming nearly solid towards the end of the operation. The product dissolves in alcohol, forming the ether $\text{P}(\text{OC}^2\text{H}^3)^3.2\text{PtCl}^2$. The deep-red solution forms no precipitate with water or with ether, but with aniline, toluidine, &c. a reaction takes place, the mixture, when heated on the water-bath and then left to cool, depositing greenish or yellowish crystals which are free from phosphorus, and consist of $\text{PtCl}^2.2\text{C}^6\text{H}^5\text{N}$ or $\text{PtCl}^2.2\text{C}^7\text{H}^7\text{N}$ respectively. The liquid separated from the crystals yields, on addition of water, a copious crystalline precipitate, consisting

of the compound $P(OC^2H^3)^3.Pt(C^6H^3NH)^2.2HCl$ or $P(OC^2H^3)^3.Pt(C^6H^3NH)^2.2HCl$ respectively.

The methylic and ethylic ethers of diphosphoplatinic chloride, $(PCl^3)^2PtCl^2$, yield with aniline and toluidine the following crystallised compounds :



Platino-tungstates and **Platino-molybdates** (W. Gibbs, *Ber.* x. 1384; *Sill. Am. J.* [3]. xiv. 61). These salts, analogous to Marignac's silico-tungstates (v. 915), are formed by boiling an acid tungstate or molybdate with platinic hydroxide.

Sodium Platino-tungstate, $10WO^3.PtO^2.4Na^2O + 25H^2O$, is obtained in this manner from sodium silico-tungstate, as a green solution, which turns red when concentrated, and ultimately deposits the salt in fine large olive-green crystals. It is easily soluble in water, and forms flocculent or indistinctly crystalline precipitates with the salts of the heavy metals and those of the higher alkaloïds.

Simultaneously with this green sodium salt, there is also produced an isomeric or metamerie compound, which separates in large crystals having a honey-yellow colour and diamond lustre, and forms the starting point of a second or yellow series of platino-tungstates. The *potassium* and *ammonium* salts of this yellow series are represented by the formulæ $10WO^3.PtO^2.4K^2O + 9H^2O$ and $10WO^3.PtO^2.4(NH^4)^2O + 12H^2O$.

Sodium Platino-molybdate, $10MoO^3.PtO^2.4Na^2O + 29H^2O$, obtained by boiling acid sodium molybdate with platinic hydroxide, likewise forms a green solution, and separates therefrom in amber-yellow tabular crystals. It dissolves readily in water, and gives precipitates with salts of the heavy metals and alkaloïds. The *silver* salt is pale green and crystalline. A second sodium salt, probably an isomeride, has likewise been obtained.

The free acids, obtained by decomposing the respective silver salts with hydrochloric acid, are greenish or yellow-green compounds.

PLEONAST. The pleonasts of Latium exhibit, according to J. Strüver (*Zeitschr. Kryst.* i. 233), the forms 0, ∞O , ∞O , 303, 202, 606, 30, 70, ∞O_3 , $50\frac{5}{2}$, among which 30, 70, ∞O_3 , 202, 606, and $50\frac{5}{2}$ are new for spinel. The crystals are rarely separate, being mostly imbedded in ejected blocks.

PLUMBOMANGANITE. A sulphide of lead and manganese (in the collection of the University of Glasgow), found in a 'pocket' in gneiss below a deposit of argentite. Sp. gr. = 4.01. Structure somewhat crystalline. Colour dark steel-grey with a bronze tinge when weathered. Easily oxidised by nitric acid, slowly attacked by boiling sulphuric and hydrochloric acids. Analysis gave 40.00 per cent. manganese, 30.68 lead, and 20.73 S, agreeing very nearly with the formula $PbS.3MnS$ (J. B. Hannay, *Mineralogical Magazine*, 1877, 149).

PLUMIERIC ACID, $C^{10}H^{10}O^5$ (A. C. Oudemans, *Liebig's Annalen*, clxxx. 154). An acid obtained from the milky juice of *Plumieria acutifolia*, an apocyanaceous shrub largely grown in Java and the other Sunda islands. The material examined by Oudemans was collected by de Vrij, who evaporated the fresh juice to dryness at 100° , and obtained 30.5 per cent. of residue consisting chiefly of an organic calcium salt, a kind of caoutchouc, and resins. To isolate the calcium salt, the substance was exhausted with petroleum-naphtha and the residue heated with dilute acetic acid, which dissolved the salt, while parts of the plant and a humus-like mass remained behind. On concentrating the solution, calcium salts of different forms separate out, all, however, containing the same acid. The free acid is obtained by converting the calcium salt into potassium plumierate, decomposing the latter with sulphuric acid, and extracting the solution with ether. It is readily soluble in alcohol and freely but slowly in ether. In cold water it dissolves but very sparingly, and from a hot solution it separates in microscopic crystals, or on slow evaporation in indistinct crusts. It melts at 139° , and decomposes at a temperature a few degrees higher, giving off first water and acetic acid, then an oily distillate having the odour of cinnamic aldehyde, while a small quantity of a crystalline substance sublimes. When the oil is oxidised, a crystalline acid is formed. On melting plumieric acid with potash, an acid is formed, giving the characteristic reactions of salicylic acid.

Plumieric acid is most probably a *methoxyl-hydroxycinnamic acid*, $C^8H^2(OH)^2(CH^2OH)(COOH)$, and forms four series of salts, according as only the carboxylic hydrogen, or in addition one or more of the three hydroxylic hydrogens, is replaced by a metal. The *tetrapotassic salt*, $C^8H^2K^4O^5 + 3H^2O$, forms monoclinic crystals, ∞P , $\infty P\infty$, and $0P$, and is very soluble and deliquescent. On dissolving

the acid in ammonia and evaporating the solution under an exsiccator, crystals of a deliquescent salt are frequently formed, which give, with silver nitrate, a precipitate containing 3 atoms of silver. On standing longer, the crystals disappear, and an amorphous residue is obtained, which is readily soluble and gives a *silver salt* containing 2 atoms of the metal. The *calcium salt*, $(C^{10}H^8O^3)_2Ca + 8H^2O$, is obtained by dissolving molecular proportions of the acid and the dicalcic salt in water and evaporating, when the salt crystallises in small hexagonal pinacoids. It dissolves in 200 pts. of water at 20° , and much more freely in boiling water. $C^{10}H^8CaO^3 + 5H^2O$ exists in the juice of the plant and forms rhombic crystals, showing the faces ∞P , $\infty \bar{P} \infty$, $\bar{P} \infty$ in OP . 1 pt. dissolves at 20° in 400 pts. of water; in boiling water it is a little more soluble, easily forming supersaturated solutions. $(C^{10}H^7O^3)_2Ca^3 + 8H^2O$ was obtained in small thick prisms by adding lime-water to a hot solution of the last salt. A salt with 10 mols. of water was once obtained by exhausting the crude calcium salt with hot water. *Silver salts*.— $C^{10}H^8Ag^2O^3 + H^2O$ is a white crystalline precipitate; $C^{10}H^7Ag^3O^3 + 1\frac{1}{2}H^2O$ is a similar body crystallising from hot water in needles.

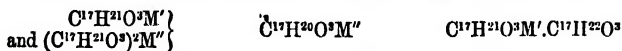
When plumieric acid is oxidised by a dilute solution of chromic acid, it is resolved into formic acid (or carbon dioxide), and the acid, $C^{10}H^8O^4$, which is very sparingly soluble in water; its *silver salt*, $C^{10}H^8Ag^2O^4$, separates from a warm solution in fibrous crystals.

When plumieric acid is heated with water and *sodium-amalgam* on a water-bath, it combines slowly with hydrogen to form hydroplumieric acid, $C^{10}H^{12}O^3$, which on evaporation of its ethereal solution, separates as a varnish, becoming crystalline on standing, and freely soluble in water.

PODOCARPIC ACID, $C^{17}H^{22}O^3$ (Oudemans, *Ber.* vii. 1122, 1125; *Liebig's Annalen*, clxx. 213). A resin-acid, forming the principal part (at least 98 per cent.) of a resin found by J. E. de Vrij in the trunk of an old tree, *Podocarpus Cupressinae*, var. *imbricata* (Blume), growing in Java. To obtain the acid, the resin is dissolved in alcohol, and the solution, mixed with as much water as can be added without producing turbidity, is left at rest for a few hours, whereupon it deposits white needle-shaped crystals, which may be nearly purified by four or five crystallisations from dilute alcohol. To obtain the acid quite pure, however, it must be converted into the sodium salt and separated therefrom.

Podocarpic acid crystallises from dilute alcoholic solution, either in thin rhombic plates exhibiting the combination $OP \cdot \infty P \cdot \infty \bar{P} \infty$, or in more massive crystals formed of a prism $\infty \bar{P} \infty$ of about 60° – 65° , the basal face OP , and several alternately developed macrolomes $\bar{P} \infty$, which produce a striated ventricose surface. It is insoluble in water, very slightly soluble in benzene, carbon sulphide, and chloroform, somewhat more soluble in dilute acetic acid, very easily in alcohol, ether, and glacial acetic acid. It is optically active, its specific rotatory power at 15° for sodium light being $+136^\circ$. It melts at 187° – 188° , and resolidifies to an amorphous glass. When heated above its melting point, it volatilises slowly, diffusing a peculiar aromatic odour. At about 130° it is resolved into its anhydride and water: $2C^{17}H^{22}O^3 = H^2O + C^{17}H^{20}O^3$, and at a higher temperature it is decomposed in the same manner as its calcium salt (*infra*), excepting that in the case of the free acid the volatile products (carpene and paracresol) occur only in traces.

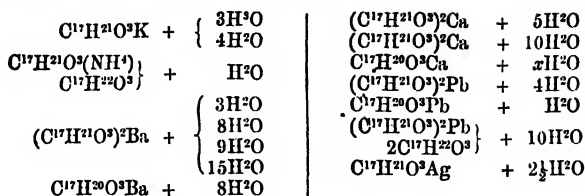
Podocarpic acid forms three series of salts, represented by the formulæ :



It decomposes the carbonates of the alkali-metals when heated therewith, forming exclusively salts of the first kind, even in presence of excess of alkali. The neutral solution of the acid in ammonia, from which silver nitrate throws down the salt $C^{17}H^{21}AgO^3$, gives off ammonia on exposure to the air, and is converted into a hyperacid salt; with the fixed alkalis similar salts could not be obtained. Of the *sodium salts*, the only one which has a constant composition is $C^{17}H^{21}NaO^3 + 7H^2O$. This salt forms long shining needles with rhombic transverse section, which give off 5 mol. water over sulphuric acid, and dissolve in about 3 pts. water at 21° . For its specific rotatory power the following values have been obtained :

In aqueous solution	Concentration 0.046	$[\alpha]_D = +82.1^\circ$
	Concentration 0.064	$[\alpha]_D = +78.8$
	Concentration 0.138	$[\alpha]_D = +73.3$
In alcoholic solution ;	Concentration 0.09	$[\alpha]_D = +86.1$

The following podocarpatos have also been analysed:



The *methylic ether*, $C^{17}H^{21}O^3(CH^3)$, prepared from the silver salt, forms small granules, easily soluble in alcohol, melting at 174° ; the *ethylic ether*, $C^{17}H^{21}O^3(C^2H^5)$, slender needles, easily soluble in alcohol and chloroform, melting at 143° – 146° .

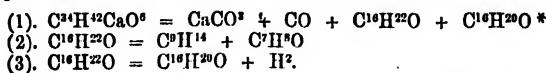
Decomposition of Podocarpic Acid by Heat.—When calcium podocarpate is subjected to dry distillation from short combustion-tubes, a tarry liquid is obtained, which, when distilled with small quantities of water as long as oil-drops continue to pass over, yields first a mobile liquid lighter than water, then a thicker liquid which sinks in water and dissolves in alkalis, whilst the greater part of the tar remains behind.

The two volatile substances, which may be completely separated by means of potash, consist of a hydrocarbon, C^9H^{14} , called *carpene*, and a cresol, which from its odour, its boiling point (202°), and the melting point (68°) of its benzoyl-derivative, appears to be *paracresol*.

Carpene is a mobile liquid which is lighter than water, smells like oil of turpentine and cinnamene, and boils at 155° – 157° . It dissolves readily in alcohol, carbon sulphide, and benzene, absorbs oxygen rapidly from the air, and is converted thereby into an amorphous resinous body ($C^{18}H^{28}O^3?$). *Monobromo-carpene*, $C^9H^{13}Br$, is formed, with evolution of HBr , on slowly mixing a solution of carpene (1 mol.) in carbon sulphide with bromine (1 mol.), also dissolved in carbon sulphide, and remains on evaporation as a syrupy liquid, stable at ordinary temperatures. *Dibromocarpene*, $C^9H^{12}Br^2$, produced by the further action of bromine, decomposes gradually, with formation of dark-coloured products. The vapours of both these bromine-compounds strongly attack the nose and eyes. The oxidation of carpene with chromic acid mixture or nitric acid does not yield terephthalic acid; whether any other aromatic acids are formed is a point not yet determined.

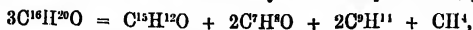
Hydrocarpol, $C^{16}H^{20}O$.—The tar which remains after the carpene and cresol have passed over, boils in a vacuum at 220° , yielding a viscid yellow strongly refracting distillate, which has a faint aromatic odour, and, when exposed to the air, gradually becomes darker without notable decomposition. This liquid is hydrocarpol; it is insoluble in water, but dissolves easily in alcohol, ether, benzene, and carbon sulphide; also in alkalis, and is separated therefrom by hydrochloric acid. When boiled with nitric acid, it yields an easily decomposable nitro-product, which has an odour of musk and crystallises from alcohol with great difficulty in brown-red granules. Hydrocarpol when distilled under ordinary pressure partly goes over unaltered, and is partly resolved at about 360° – 400° into carpene, metacresol, and small quantities of a solid phenolic substance, which makes its appearance towards the end of the distillation. The same products are obtained from the original tarry residue if it be distilled under ordinary pressure instead of in a vacuum: hence this tarry matter consists mainly of hydrocarpol. The solid phenolic body, methanthrol, $C^{16}H^{20}O$, melts at 122° .

Free podocarpic acid when heated is first resolved at about 330° into water and the anhydride $C^{16}H^{20}O^3$. On continuing the heat, the same products are obtained as from the calcium salt, excepting that the volatile products, carpene and metacresol, are obtained only in traces. The gases formed at the same time consist of CO^2 (rather more than 1 mol. to 1 mol. of the anhydride), CO (about 0.7 mol. to the same quantity), and methane. Oudemans thinks it probable that in the distillation of calcium podocarpate there is first formed a phenol, $C^{16}H^{20}O$, together with hydrocarpol, $C^{16}H^{20}O$, and that this phenol is then resolved partly into carpene and paracresol, partly into hydrogen (which is given off in the form of water) and hydrocarpol, which forms by far the largest portion of the product. These reactions may be represented by the following equations:



* The same equation, with omission of CaO , will apply to the decomposition of podocarpic anhydride, $C^{16}H^{20}O^3$.

The methanthrol, $C^{15}H^{12}O^2$, is formed by a secondary reaction, probably thus



which likewise accounts for the occurrence of methane.

Podocarpic acid, distilled with *zinc-dust*, yields methanthrene, $C^{15}H^{12}$ (p. 1301).

Nitropodocarpic Acids. By the action of nitric acid on podocarpic acid two nitro acids are produced, which also form with the alkalis salts containing 1 and 2 atoms of metal; the monometallic salts are of a fine red colour; the bi-metallic salts are honey-yellow and less stable. The ammonium salts readily give off the whole of their ammonia.

Mononitropodocarpic acid, $C^{17}H^{21}(NO^2)O^3$, is best prepared by prolonged heating of podocarpic acid with dilute nitric acid (1 pt. nitric acid, sp. gr. 1.34 to 5 or 6 pts. water). It forms small irregular crystals, insoluble in water and in carbon sulphide, very slightly soluble in chloroform and benzene, sparingly in cold, somewhat more freely in boiling alcohol, melting at 205° . The *dipotassium salt*, $C^{17}H^{19}(NO^2)O^3K^2 + 5\frac{1}{2}H^2O$, crystallises only from solutions containing excess of alkali, in red needles with green reflex, easily soluble in water and in alcohol. The *monopotassium salt* exists only in alcoholic solution, being decomposed, on evaporation or on addition of water, into the free acid and the dipotassium salt. The *disodium salt*, $C^{17}H^{19}(NO^2)O^3Na^2 + 9H^2O$, forms cinnabar-red laminae, easily soluble in water and in alcohol. The *diammonium salt*, $C^{17}H^{19}NO^2O^3(NH^4)^2 + 4H^2O$, forms garnet-red monoclinic crystals, which are decomposed by contact with the air and by water. The *monobarium salt*, $C^{17}H^{19}(NO^2)O^3Ba + 7H^2O$, is obtained in red needles an inch long, on cooling a mixture of the warm solutions of the dipotassium salt and barium chloride. It also crystallises with 3 mols. water in small brown spherical groups, or is precipitated on adding barium chloride to a very strong solution of the nitro-acid in ammonia, as a fine dark carmine-coloured powder, which, while suspended in the liquid, gives it the appearance of arterial blood. The *hemibarium salt*, $[C^{17}H^{20}(NO^2)O^3]^2Ba + 4H^2O$, forms yellow needles, sparingly soluble in water and in cold alcohol. The *monocalcium salt*, $C^{17}H^{19}(NO^2)O^3Ca + 4H^2O$, crystallises in slender orange-red needles, nearly insoluble in water.

Dinitropodocarpic acid, $C^{17}H^{20}(NO^2)^2O^3$, is produced by cautiously heating podocarpic acid with nitric acid of sp. gr. 1.34, or in a state of greater purity, by boiling sulphopodocarpic acid with nitric acid. It forms pale yellow crystals similar in shape to those of potassium ferrocyanide, but probably belonging to the orthorhombic system. It is insoluble in water, sparingly soluble in chloroform, benzene, and carbon sulphide, moderately soluble in alcohol. Melts at 203° . Becomes brownish in sunshine. The *dipotassium salt*, $C^{17}H^{18}K^2(NO^2)^2O^3 + 5H^2O$, crystallises only in presence of free alkali. It is very soluble. The *monobarium salt*, $C^{17}H^{18}Ba(NO^2)^2O^3 + 4H^2O$, separates from a moderately concentrated ammoniacal solution of the dinitro-acid mixed with barium chloride, in shining, brown-red, strongly polarising rhombic laminae. It is nearly insoluble in water and in alcohol. The *diargentic salt*, $(C^{17}H^{18}Ag^2(NO^2)^2O^3 + 4H^2O)$, is precipitated by silver nitrate from a boiling solution of the barium salt in orange-red coloured flocks.

Amidopodocarpic Acids are formed by treating the nitro-acids in alcoholic solution with tin and hydrochloric acid, but they are very unstable, and have not been obtained in a state of purity. *Hydrochloride of monoamidopodocarpic acid* has the composition $C^{17}H^{21}(NH^2)O^3.HCl + \frac{1}{2}H^2O$.

Sulphopodocarpic Acid, $C^{17}H^{21}(SO^3H)O^3$, is formed by gently heating podocarpic acid with 3 pts. sulphuric acid. On adding water, the unaltered podocarpic acid separates out, and the sulpho-acid remaining in solution may be freed from excess of sulphuric acid by means of baryta. The red aqueous solution of sulphopodocarpic acid exhibits a splendid fluorescence, red, blue, or emerald-green, according to the particular conditions of the preparation. The solution of the *pure acid* is not fluorescent; it dries up in the exsiccator to an amorphous mass having the composition $C^{17}H^{21}(SO^3H)O^3 + 8H^2O$. Even very dilute solutions of this acid give, when boiled with traces of nitric acid, a precipitate of dinitropodocarpic acid.

Sulphopodocarpic acid is a strong acid, and forms two series of salts. The *disodium salt*, $C^{17}H^{19}Na^2(SO^3H)O^3 + 7H^2O$, forms rosettes of easily soluble crystals. The *monobarium salt*, $C^{17}H^{19}Ba(SO^3H)O^3 + 8H^2O$, crystallises in white laminae, unctuous to the touch, very soluble in boiling water and alcohol, less soluble in cold water. The *hemibarium salt*, $[C^{17}H^{20}(SO^3H)O^3]^2Ba + 3H^2O$, prepared by treating the preceding salt with acetic acid, is much less soluble. The *monocalcium salt*, $C^{17}H^{19}Ca(SO^3H)O^3 + 7H^2O$, forms thin laminae, for the most part concentrically grouped.

Ethylbromopodocarpic Acid, $C^{17}H^{20}(C^2H^5)BrO^3$. When bromine (2 mols.) is added to podocarpic acid (1 mol.) immersed in carbon sulphide, streams of hydrogen

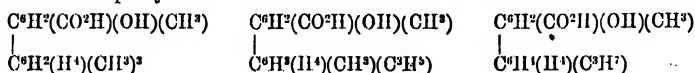
bromide are given off, and the resulting bromo-substitution-product dissolves in the liquid; but the solution when evaporated leaves a residuo which cannot be made to crystallise. When, on the other hand, solutions of podocarpic acid and bromine in ether containing alcohol are mixed together, the mixture, which becomes warm and soon loses its colour, leaves on evaporation a resinous residuo which suddenly becomes crystalline. The product thus obtained separates from warm alcohol in rather large shining crystals consisting of an *alcoholate* of *ethylbromopodocarpic acid*, $C^{17}H^{20}(C^2H^5)BrO^3.C^2H^4O$. This compound melts at a temperature above 80° , and after prolonged heating leaves ethylbromopodocarpic acid as a white crystalline powder, which melts at 158° , and forms with alkali-solutions salts which dry up to gelatinous masses.

Acetylpodocarpic Acid, $C^{17}H^{21}(C^2H^3O)O^3$, formed by the action of acetyl chloride on podocarpic acid, crystallises in small needles, melts between 150° and 152° , and resolidifies to a transparent resin.

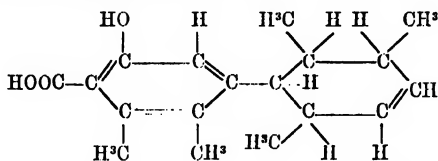
Constitution of Podocarpic Acid.—From the formation of the substitution-derivatives above described, and from its mode of decomposition when heated alone, and with zinc-dust, Oudemans infers that the constitution of podocarpic acid may be most simply represented by the formula :



moreover, that the radicle C^9H^{13} is most probably an addition-product of benzene, so that this formula may be resolved into one of the following, which represent it as a derivative of diphenyl :



The resolution of calcium podocarpate by heat into $CaCO^3$, C^9H^{14} , and C^7H^4O may perhaps be most readily explained by assigning to podocarpic acid the structure represented by the following formula :



The formation of paracresol by the decomposition of podocarpic acid shows that the radicles OH and CH^3 must be in the relative positions 1 : 4.

PODOPHYLLUM. On the constituents of *Podophyllum peltatum*, see W. C. Busch (*Pharm. J. Trans.* [3], viii. 424; *Chem. Soc. J.* xxxiv. 325). On the Colour of Podophyllum resin, as affected by its state of aggregation, see Senier a. Lowe (*Pharm. J. Trans.* [3], viii. 443; *Chem. Soc. J.* xxxiv. 326). According to F. B. Power (*Pharm. J. Trans.* [3], v. 244), the resin extracted from podophyllum by alcohol may be separated into two different substances, one of which is soluble in ether, the other insoluble. The soluble portion acts on the organism much more powerfully than that which is insoluble in ether.

POLYDYMITE. A native sulphide of nickel, crystallising in the regular system, in octohedrons which are polysynthetically twinned, the twin-plane being a face of the octohedron. Most of the crystals are tabular, through predominance of the face parallel to the twin-plane, and there are also prismatically developed octohedrons. Cleavage incompletely cubical. Fracture uneven to conchoidal. Hardness = 4-5. Sp. gr. 4.808-4.816. Somewhat sectile. Colour on freshly broken surfaces light steel-grey, becoming very soon dark-grey or yellow. Decrepitates before the blowpipe; fuses on charcoal to a blackish-green magnetic bead. Dissolves in nitric acid with separation of sulphur; does not dissolve in hydrochloric acid, but enclosed bismuth-glance is dissolved out by this acid. Strong metallic lustre. Chemical composition as follows :

Ni	Co	Fe	S	As	Sb
53.508	0.606	3.844	40.270	1.041	0.508 = 99.777

This analysis leads to the general formula, R^4S^3 . Polydymite is found in veins of other ores at Sayn-Altenkirchen, accompanied by millerite, bismuth-glance, zinc-blende,

gersdorffite, and ullmannite, lying on a layer of spathic iron and quartz. On one specimen the crystals were found to have lost their metallic lustre, and to have been converted into a reddish-brown substance. On breaking some of these pseudomorphs, it was observed that they were penetrated by fresh acicular millerite. A careful examination of these crystals leads to the inference that the polydymite and millerite were formed simultaneously (H. Laspeyres, *J. pr. Chem.* [2], xiv. 397; *Jahrb. f. Min.* 1876, 737; 1877, 296).

POLYHALITE. This mineral, from Stebnik in Galicia, has been analysed by M. v. Lill. A. gives the direct results of analysis; B. the corrected values, after deduction of ferric oxide and sodium chloride:

	CaSO ⁴	MgSO ⁴	K ² SO ⁴	NaCl	Fe ² O ³	H ² O
A.	44.47	20.22	27.14	1.61	0.04	6.25 = 99.73
B.	45.22	20.56	27.60	—	—	6.35 = 99.73

G. Krause (*Arch. Pharm.* [3], vi. 325) has analysed polyhalite from Stassfurt, with the following results, A. and B. denoting as above:

	CaSO ⁴	MgSO ⁴	K ² SO ⁴	NaCl	Insol.	H ² O
A.	32.53	13.11	24.82	18.17	0.95	10.58 = 100.16
B.	40.14	16.17	30.62	—	—	13.05 = 99.98

POLYMERISM. On Physical Polymerism and Isomerism, see O. Lehmann (*Zeitschr. Kryst.* 1877, i. 97-131; *Jahresb. f. Chem.* 1877, 31-40).

On the influence of Polymerisation on Chemical Compounds, see J. Löwenthal (*Chem. Centr.* 1877, 193; *Chem. Soc. J.* xxxiv. 108).

POLYMORPHISM. On the polymorphism of Elementary Bodies, see R. Hermann (*J. pr. Chem.* [2], xvii. 289; *Chem. Soc. J.* xxxiv. 702).

POLYPORUS. G. Fleury (*Pharm. J. Trans.* [3], vi. 869) found in *Polyporus officinalis* the following constituents:

Water	9.200
Resin and Agaric acid	60.584
Another resin with Magnesium Sulphate	7.282
Resinous body with Lime and Magnesia	2.514
Nitrogenous substance with Salts	1.900
Oxalates, Malates, and Phosphates of Calcium and Iron	1.058
Nitrogenous substance, soluble in Potash	7.776
Fungin	9.686

100

POLYPORIC ACID, C⁶H⁷O² (C. Stahl Schmidt, *Liebigs Annalen*, clxxxvii. 177). An acid contained in a fungus belonging to the genus *Polyporus*, which grows on the bark of diseased or dead oaks: it occurs in large quantity, amounting to 43.5 per cent. of the dry fungus. The fungus is semicircular, and rests directly on the bark without a stalk; it is of an ochre-yellow colour when dry, brownish-yellow in the moist state, and is coloured deep violet by dilute ammonia, whence Stahl Schmidt proposes to call it *Polyporus purpuraceus*. The violet coloration is due to the formation of ammonium polyporate.

To prepare the acid, the fungus is washed with water, and then steeped in dilute ammonia for twenty-four hours. By this means the acid is converted into its ammonium salt, which is soluble in water, though the acid itself is totally insoluble. The ammonium polyporate is next decomposed by hydrochloric acid, and the precipitated acid, after filtering and washing, is treated with caustic potash, and thus converted into potassium polyporate, which is washed for some time with caustic potash, in which it is insoluble. It is then washed with alcohol till free, as far as possible, from potash, and dissolved in hot water. Carbon dioxide is passed into the liquid to convert any remaining traces of potash into the carbonate, and it is then crystallised several times. The polyporic acid is finally precipitated by hydrochloric acid.

Polyporic acid has the colour of the fungus, and is totally insoluble in water, so that the slightest trace of a soluble polyporate shows a turbidity on addition of an acid. The soluble polyporates might, therefore, be used as indicators in alkalimetry. The acid is also insoluble in ether, benzene, bisulphide of carbon, and acetic acid. It dissolves very slightly in chloroform, amyl alcohol, and boiling (95 per cent.) ethyl alcohol. From the latter solvent it crystallises in small rhombic plates, which exhibit a lively bronze colour when dry. It contains no water of crystallisation, and becomes strongly electrical when rubbed in the dry state. It may be heated without change to 220°, but at a higher temperature it melts, and sublimes with partial

decomposition, evolving a smell of heated or burning oak-branches, and after a while that of bitter almond oil.

Reactions.—1. When polyporic acid is added to a cold mixture of potassium chlorate and hydrochloric acid, it is converted into a bright-yellow compound, soluble in alcohol; but if the acid is added to boiling hydrochloric acid, and potassium chlorate is introduced little by little, an oily body gradually forms at the bottom of the vessel, becoming solid on cooling. This body is partly soluble in boiling water, and the solution deposits snow-white feathery crystals easily soluble in caustic potash, and apparently consisting of a chlorinated acid (34.5 per cent. Cl). The part which is insoluble in water dissolves easily in alcohol, and crystallises with great facility in long slender needles of a golden-yellow colour. Heated with caustic potash, it evolves a smell of bitter almonds, and forms a dark-red substance totally insoluble in alcohol, ether, alkalis, &c. The yellow compound (containing 38.7 per cent. of chlorine) is decomposed on heating, and emits a smell of benzoyl chloride. A third body is found in the alcoholic mother-liquor of the original solution, and remains behind as a thick oil on evaporation of the alcohol.

2. When potassium polyporate is boiled for some time with excess of concentrated caustic potash, the violet colour of the solution gives way to a yellowish-red, and the smell of bitter almonds becomes perceptible. On cooling, fine colourless needles are deposited. The alkaline solution becomes turbid on addition of hydrochloric acid, and on standing a dull-yellow body separates, which is soluble in alcohol, and unites with alkalis.

3. Addition of zinc-dust to an alkaline solution of potassium polyporate renders the solution colourless, but it becomes red again on exposure to air. When ammonium polyporate, mixed with excess of ammonia, is left at rest, a decomposition or alteration of the acid takes place, and the liquid becomes blue and fluorescent. At a higher temperature the change takes place more quickly, and a brown insoluble body is formed.

4. By heating potassium polyporate to a high temperature with zinc-dust, benzene is produced, a reaction which when viewed in connection with the behaviour of the acid to caustic potash, points to the conclusion that polyporic acid belongs to the aromatic group.

Salts of Polyporic Acid.—Polyporic acid forms salts with all the bases. The easily soluble salts—those of the alkali-metals and ammonia—form violet solutions, which cannot be distinguished in appearance from a concentrated solution of potassium permanganate. All the salts are decomposed by the stronger acids, even by acetic acid, at ordinary temperatures, with perfect separation of the polyporic acid; but when polyporic acid is boiled with potassium or sodium acetate, the acetic acid is expelled, and a polyporate is formed. All the polyporates, except that of ammonium, can be heated above 200°, without decomposition.

Potassium polyporate, $C^9H^6O^2K + H^2O$, crystallises in the form of gypsum. It does not give off its water of crystallisation when dried over sulphuric acid, but loses it completely when heated to 120°. The **sodium salt**, $C^9H^6O^2Na + H^2O$, obtained by neutralising the acid with dilute caustic soda, is insoluble in concentrated caustic soda, and loses its water of crystallisation at 180°. The **ammonium salt**, $C^9H^6O^2NH^4 + H^2O$, loses not only its water of crystallisation, but also the whole of its ammonia, by long standing in the air, or by heating to 100°. The **barium salt**, $(C^9H^6O^2)^2Ba + 4H^2O$, loses 2 mols. of water at 120°, and the other two at 150° to 160°. If the salt containing 4 mols. of water is boiled for a time, another salt is precipitated, which has the composition $(C^9H^6O^2)^2Ba + 2H^2O$. This is also quite insoluble in water, has a metallic lustre, and loses its water of crystallisation at 180°. The **strontium salt**, $(C^9H^6O^2)^2Sr + 4H^2O$, is insoluble in water. It is not altered by boiling, but is converted by a heat of 120° into a salt of the composition $(C^9H^6O^2)^2Sr + H^2O$. It loses the last molecule of water at 180°–200°. The **calcium salt**, $(C^9H^6O^2)^2Ca + 3H^2O$, is slightly soluble in water. At 120° it loses 2 mols. of water, and leaves a salt of the composition $(C^9H^6O^2)^2Ca + H^2O$. At 180° it becomes anhydrous. The **magnesium salt**, $(C^9H^6O^2)^2Mg + 3H^2O$, is so sparingly soluble that ammonium polyporate can be used for the separation of magnesia from the alkalis. The **silver salt**, $C^9H^6O^2Ag$, is quite insoluble in water, and cannot be distinguished in appearance from the acid itself. It is anhydrous, and undergoes no change by boiling with water or heating to 150°. All the other metallic polyporates are insoluble amorphous precipitates.

Methyl polyporate, $C^9H^6O^2.CH^3$, obtained by the action of methyl iodide on silver polyporate, may be crystallised from boiling alcohol of 95 per cent.; it melts at 187°, and is decomposed by heating with potash or ammonia, yielding the corresponding polyporate. The **ethyl ether**, prepared in like manner, melts at 134°.

Acetopolyporic acid, $C^6H^4O^2.C^2H^2O$, is formed when polyporic acid is heated to 150° – 170° in closed tubes, with excess of acetic anhydride. It melts at about 205° .

Polyporic acid is violently acted on by concentrated nitric acid, but the products of the reaction have not yet been fully investigated.

POLYTHIONIC ACIDS. See SULPHUR, OXYGEN-ACIDS OF.

POLYTHYMOQUINONE. See THYMOQUINONE.

POMEGRANATE, ALKALOIDS OF (Tanret, *Compt. rend.* lxxxvi. 1270; lxxxvii. 358; lxxxviii. 716; *J. Pharm.* [4], xxviii. 384). 1. *Pelletierine*, $C^9H^{15}NO$. This base, which appears to be the tannic principle of the pomegranate, is prepared as follows: The bark of the tree is roughly powdered, and mixed with milk of lime to a thick paste, which is washed with water; the liquid is shaken with chloroform; and the chloroform solution is treated with a dilute acid, whereby a salt of pelletierine is formed, from which the free base may be separated by treatment with potassium carbonate and agitation with chloroform, the resulting solution, when evaporated, leaving the base as a colourless oily mass boiling at about 180° . It may be purified by dissolving it in ether, distilling the ethereal solution in a current of hydrogen, keeping the residue at a temperature from 130° – 140° , until water is no longer given off, and then raising the heat to 180° – 186° , at which the alkaloïd begins to distil. It is thus obtained as a colourless liquid, which quickly becomes coloured in the air. Its sp. gr. is 0.999 at 0° , and 0.985 at 21° . It dissolves in water, with contraction, a mixture of 1 pt. of pelletierine and 2.5 pts. of water having a sp. gr. = 1.021 at 21° . The alkaloïd is dextrogyrate, its power of rotation $[\alpha] = +8$, and in the form of the pure sulphate $+15.9$. With potassium dichromate and sulphuric acid it gives a deep green coloration. With hydrochloric acid it fumes like ammonia.

Pelletierine is a mono-acid base, the formula of its hydrochloride being $C^9H^{15}NO.HCl$, and that of its sulphate $(C^9H^{15}NO)^2H^2SO^4$. Its salts are very hygroscopic, pure white when crystallised in dry air, otherwise coloured; they have a faint odour of the base, easily become acid, and have a bitter and aromatic taste.

2. Pomegranate bark contains three other volatile alkaloïds, which may be separated in the following manner. The powdered bark is mixed with milk of lime and treated with water; and the solution is shaken with chloroform, which in its turn is shaken with a dilute acid. A solution containing a mixture of the alkaloïds is thus obtained, which is dextrogyrate, lævogyrate, or inactive, according to the bark used. To separate these alkaloïds, the solution is treated with sodium bicarbonate and saturated with carbonic anhydride; it is then shaken with chloroform, and the latter with dilute sulphuric acid. This solution, which is dextrogyrate, contains the sulphate of a dextrogyrate liquid alkaloïd and of an inactive solid alkaloïd.

By treating the solution in a similar manner, but using caustic soda instead of sodium bicarbonate, a lævogyrate solution is obtained, which, after evaporation in a vacuum over sulphuric acid, leaves a crystalline sulphate of a lævogyrate liquid base, and an uncrystallisable sulphate of an inactive base. These may be separated by filtration. The active sulphate possesses the rotatory power $[\alpha]_D = -30^{\circ}$.

Crystalline Base.—By decomposing with an alkali the dextrogyrate solution above described, treating the product with chloroform, and evaporating off the latter, crystals are obtained, which may be purified by recrystallisation. From an aqueous solution, prismatic crystals are deposited, having the formula $C^9H^{15}NO + 4H^2O$. The hydrated base melts at 46° , but can be cooled to 37° without solidifying. It boils at 246° , and is soluble in alcohol, ether (9 pts. at 10°), water (2.5 at 10°), and chloroform, which extracts it from its aqueous solution. It is a strong base, expelling ammonia from its salts, and precipitating alumina, baryta, and lime, but not magnesia. It gives all the characteristic reactions for the alkaloïds, and with sulphuric acid and potassium dichromate gives, like pelletierine, a deep green colour.

The *hydrochloride*, $C^9H^{15}NO.HCl$, crystallises in rhombohedrons, and is soluble in its own weight of water at 10° . The *sulphate*, $C^9H^{15}NO.HSO^4 + 4H^2O$, crystallises with 4 mols of water, which it loses over sulphuric acid. At 10° it is soluble in less than twice its weight of water. The *platinochloride* $(C^9H^{15}NO.HCl)^2.PtCl^4$, crystallises in reddish-yellow needles.

A base called *granatine* is mentioned by Durand (*J. Pharm.* [4], xxviii. 168) as obtained from dried pomegranate bark which had been kept for a year.

POONAH-LITE. A variety of scolecite occurring, together with apophyllite, in melaphyre-conglomerate, at Poonah in India. Its analysis (A) agrees with the scolecite formula, $CaO.Al^2O^3.3SiO^2 + 3H^2O$ (B).

	SiO ²	Al ² O ³	CaO	Na ² O	K ² O	H ² O
A.	46.91	26.93	13.33	0.22	0.08	13.83 = 100.40
B.	45.80	26.21	14.25	—	—	13.74 = 100

(Petersen, *Jahrb. f. Min.* 1873, 852).

POPLAR. The buds of several species of poplar yield by distillation a volatile oil, the greater part of which boils at 260° – 261° , and agrees in composition with the formula C^8H^8 (Picard, *Ber.* vi. 1160).

On *Chrysin* and *Methyl-chrysin*, or *Tecto-chrysin*, obtained from poplar buds, see p. 465 of this volume. *Populin* and *Salicin* have also been obtained from these buds (Picard).

POPPY. According to Hesse (*Lieb. Ann.* clxxxv. 329), the milky juice of the unripe capsules of the red poppy (*Papaver Rhæas*) leaves on evaporation about 34 per cent. of dry matter, in which no trace of morphine or any similar alkaloid can be detected. It contains, however, 2.1 per cent. *rhæadine*, and traces of other partially crystallisable alkaloids.

The composition of the ash of poppy-petals has been determined by C. J. Warden (*Chem. News*, xxxiv. 27) with the following results, after deduction of CO_2 , sand and charcoal:

K ² O	KCl	NaCl	CaO	MgO	Fe ² O ³	Al ² O ³	SO ²	P ² O ⁵	SiO ²	
41.76	12.29	1.21	10.72	5.61	3.86	1.23	3.85	5.61	13.86	= 100

On *Respiration in the Ripening Fruits of the Poppy*, see PLANTS (p. 1640).

PORCELAIN. Remarks on the structure of porcelain have been made by H. Behrens (*Pogg. Ann.* cl. 386). He considers that, in the firing of porcelain, only the quartz-grains in the mixture remain unaltered, whilst all the other constituents are fused at the high temperature of the furnace, and partly yield products of devitrification. The translucent Japanese porcelains have essentially the same quantitative composition as the European, but the undecomposed vitreous mass predominates in them.

According to Salvétat (*Moniteur de la Céramique*, 1873, No. 11; *Dingl. pol. J.* ccix. 468), porcelain is so porous that its entire mass may be coloured by prolonged contact with the solution of a colouring matter. Porcelain which had stood for some days with its unglazed foot in a solution of fuchsine, exhibited in reflected light the white colour of the glaze, but appeared of a fine red by transmitted light.

On the preparation and composition of Japanese porcelain, see H. Wurtz (*Amer. Chemist*, vii. 218). On the history and manufacture of Chinese porcelain: A. Heintz (*Dingl. pol. J.* ccxxi. 156).

PORPHYRY. The porphyries of Lago Lugano have been examined by B. Studer (*Jahrb. f. Min.* 1875, 881). The following are analyses of a red porphyry (A) and a black porphyry (B) from the railway-tunnel near Maroggia: 1. Analyses by Schwarzenbach. 2. By v. Fellenberg. 3. The same, corrected, after deduction of bases (as carbonates) extractable by cold acids.

	SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	MnO	K ² O	Na ² O	X ⁽¹⁾	Y ⁽²⁾
A. 1.	74.71	11.27	4.345	1.64	0.36	—	3.89	—	3.69	—
2.	71.74	12.60	2.45	2.30	1.24	0.84	4.14	3.41	3.50	—
3.	70.18	12.33	2.40	0.38	0.26	0.82	4.05	3.84	0.93	5.31
B. 1.	65.47	15.15	10.64	1.61	0.34	—	3.65	—	3.10	—
2.	61.67	16.38	6.31	2.57	3.02	0.30	4.22	3.65	3.31	—
3.	60.80	16.15	6.22	0.62	2.48	0.30	4.16	3.60	1.23	4.44

(¹) Water or Loss by Ignition.

(²) Carbonates.

Sp. gr. according to v. Fellenberg: A = 2.645; B = 2.6598 at 15° .

The mineralogical composition of these porphyries has been calculated by v. Fellenberg from his own analyses, with the following results: 1. With the carbonates; 2. After deduction thereof.

	A 1.	A 2.	B 1.	B 2.
Orthoclase	33.78	35.67	59.21	61.03
Oligoclase	27.01	28.53	30.35	31.29
Quartz	30.76	32.39	—	—
Magnetic Iron oxide	—	—	6.22	6.41
Ferrie oxide	2.40*	2.53	—	—
Water	0.93	0.98	1.23	1.27
Carbonates	5.31	—	4.44	—
	100.19	100	101.45	100

The following are analyses of porphyry from various localities: (1-5) from the Vicentine (A. v. Lasaulx, *Min. Mitth.* 1873, 70): 1. *Non-quartziferous Porphyry* from Pieve. Sp. gr. 2.59. (2). *Porphyrite* from the Guizzo di Schio. Sp. gr. 2.67. (3). *Porphyry* from Fongara. The indurated argillaceous ground-mass contains felspar and mica, but no quartz. Sp. gr. 2.586. (4). Decomposed rock from the Rasta del Recoaro, probably a decomposition-product of No. 3. Sp. gr. 2.589. (5). *Pitchstone-porphyry* from La Rasta. Sp. gr. 2.466.

(6-8). From the neighbourhood of Roanne, Loire, France (A. Guyardet, *Bull. Soc. Chim. geol.* [3], i. 499). 6. *Porphyry* from Saint-Just-en-Chevalet. The orthoclastic ground-mass encloses large orthoclases, small oligoclases, black mica, and very frequently lamellæ of a green tale (pinitoid?). Sp. gr. 2.23. 7. *Porphyry* from Boen-sur-Ligron. The felspathic ground-mass (probably oligoclase) encloses oligoclase, numerous black micas, tale (pinitoid), and rarely quartz crystallised in double pyramids. Sp. gr. 2.85. 8. Grey porphyritic *Kurite* from La Bombarde near St. Romain d'Urfé. The ground-mass, probably anorthite, encloses anorthite, oligoclase, hornblende, and quartz. Sp. gr. 2.17.

9. From Rockhampton in Queensland (Daintree, *Geol. Soc. Qu. J.* xxviii. 271).

10. *Hornstone-porphyry* of the Salband from the vein in the Kestenthalrücken in the Harz. Sp. gr. 2.697-2.701. 11. Rock resembling *granite-porphyry* from the middle of the vein. Sp. gr. 2.68 (Lossen, *Zeitschr. geol. Ges.* 1874, xxvi. 856).

12. *Granite-porphyry* from Boucha, near Leipzig. 13. The same from Altenberg, in the Erzgebirge (Baranowski, *Zeitschr. geol. Ges.* xxvi. 522).

(14-15). *Porphyry* from Muldenstein, between Bitterfeld and Jessnitz (E. Reichardt, *Arch. Pharm.* [3], v. 310). 14. Solid rock, greyish-white, with rusty spots on the fractured surfaces. 15. The same weathered and easily crumbled.

(16, 17). From South Tyrol (C. v. Hauer, *Ver. geol. Reichsanst.* 1875, 331). 16. *Red orthoclase-porphyry* from the Canzacoli, near Predazzo. 17. The same from Canon, near Predazzo.

18. *Mica-porphyry* from Rohrbach, in the Black Forest of Baden. The dense ground-mass encloses specks of blackish-green mica. 19. *Hornstone-porphyry* from Kesselberg, in the Black Forest; analysis by F. Geremont: *a.* Total analysis; *b.* Portion soluble in hydrochloric acid. 20. *Porphyritic rock* near St. Märgen, in the Black Forest; analysed by E. Meisinger: *a* and *b* as above (Vogelgesang, *Jahresb. f. Chem.* 1873, 1213).

	SiO ²	TiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	MgO	CaO	K ² O	Na ² O	P ² O ⁵	CO ²	X (%)	
1	61.07	—	18.56	2.60	—	—	1.08	2.86	6.83	3.18	—	1.36	2.13	= 99.67
2	60.86	—	14.62	7.91	—	—	1.96	3.18	3.26	3.92	—	2.11	2.95	= 100.77
3	64.78	—	14.44	5.46	—	—	1.20	2.35	4.63	0.83	—	2.32	3.86	= 100.37
4	42.25	—	4.52	8.76	—	—	0.48	18.27	6.38	0.99	—	15.85	1.43	= 98.93
5	62.02	—	16.16	5.25	—	—	0.94	5.39	1.18	2.92	—	1.08	4.91	= 99.85
6	62.30	—	19.70	—	3.78	—	1.10	4.50	3.45	2.57	—	0.70	1.62	= 99.72
7	68.30	—	15.60	—	7.47	—	1.60	2.60	0.19	1.70	—	—	2.23	= 99.69
8	64.00	—	18.00	—	5.40	—	3.60	4.30	0.80	1.60	—	—	1.90	= 99.60
9	61.43	—	20.29	1.22	3.26	—	1.57	3.23	1.69	6.17	—	—	1.03 (*)	= 99.89
10	72.30	0.11	15.04	0.64	1.28	—	0.59	1.59	4.95	1.02	0.19	—	2.18	= 98.99
11	70.40	0.28	15.29	0.09	1.69	—	0.58	1.62	3.89	4.09	0.22	—	1.13	= 99.28
12	66.3	—	15.4	7.0	—	—	1.5	2.3	4.4	3.5	trace	—	0.8	= 101.2
13	67.1	—	12.1	8.7	—	—	1.6	2.5	5.3	2.4	trace	—	0.6	= 100.3
14	77.48	—	17.10	2.83	—	0.84	0.10	0.38	1.03	0.13	trace	—	—	= 99.89
15	75.73	—	21.92	0.98	—	0.18	0.10	0.27	0.55	0.08	—	—	—	= 99.81
16	64.45	—	16.31	6.49	—	trace	0.30	1.10	5.45	5.00	—	—	0.82	= 99.92
17	70.09	—	15.55	4.02	—	trace	0.41	0.57	5.82	2.94	—	—	0.61	= 100.1
18	63.76	—	16.19	4.10	1.12	0.36	2.56	3.32	3.74	1.73	—	1.53	1.79	= 100.14
19a	84.12	—	9.38	1.78	—	—	0.01	0.08	0.85	0.23	—	0.14	3.68	= 100.29
19b	2.76	—	1.94	1.78	—	—	0.01	0.08	0.34	—	—	0.14	—	= 7.05
20a	57.61	—	18.45	7.69	—	0.26	0.25	4.02	5.47	2.93	—	0.72	2.28	= 99.68
20b	5.24	—	3.52	7.15	—	0.19	0.13	1.75	1.86	2.12	—	0.72	—	= 22.08

(*) Loss by ignition.

(*) Water: 0.725 combined; 0.300 hygroscopic.

The granitic porphyrites of Saxony, occurring near Altenberg in the Erzgebirge, near Beucha, in the neighbourhood of Leipzig, and on the Tammelberg, have been described and analysed by Baranowski (*Jahrb. f. Min.* 1875, 199). The ground-mass of these porphyries, which are perfectly identical, consists of separate grains of quartz, felspars, hornblende, and chlorite, associated with magnetic iron oxide and apatite. Among the microscopic constituents, quartz and felspar are especially abundant. The occurrence of quartz in the pyramidal form in the granular ground-mass is characteristic of the granite-porphyries. The quartz is further distinguished by the numerous microscopic enclosures, partly vitreous, partly liquid, which it contains. The large crystals of orthoclase are accompanied by small plagioclases. Especially remarkable is the occurrence of vitreous particles, enclosed in the felspars, inasmuch as such enclosures, though known to occur in the felspars of trachyte and quartz-porphyry, have not hitherto been observed in granites. Hornblende and chlorite

must also be enumerated as essential constituents of the granite-porphyrries. The chlorite is evidently a transformation-product of the hornblende, inasmuch as crystals are found, consisting of a layer of chlorite enclosing a nucleus of hornblende. Magnetic iron oxide appears in thin sections of the rocks in small isolated octohedrons, more frequently in granules irregularly distributed through the mass. Lastly, the presence of apatite is remarkable, since this mineral has hitherto been found more frequently in basic rocks than in those which are rich in quartz.

The following are analyses of two granitic porphyries: *a*, from Beucha; *b*, from Altenberg:

	SiO ^a	Al ^a O ^a	Fe ^a O ^a	CaO	MgO	K ^a O	Na ^a O	H ^a O
<i>a.</i>	66.3	15.4	7.0	2.3	1.5	4.4	3.5	0.8 = 101.2
<i>b.</i>	67.1	12.1	8.7	2.5	1.6	5.3	2.4	0.6 = 100.3

A microscopic examination of the porphyrites of Ilefeld by A. Streng (*Jahrb. f. Min.* 1875, 623) shows that these rocks are composed of a fine-grained ground-mass consisting of orthoclase, plagioclase, small quantities of hornblende and quartz, magnetic iron oxide, a small quantity of apatite, sometimes also graphites, titanite iron and specular iron, or pyrolusite, and enclosing porphyritically separated plagioclase, hornblende (often apparently formed from augite), quartz, titanite iron, graphite, magnetic iron oxide, and accessorially garnet, more rarely iron pyrites. These porphyrites, therefore, are intermediate between the quartz-porphyrries and the melaphyres (p. 1272).

POSIDONIA OCEANICA. This plant, used as manure, has been examined by F. Sestini (*Gazz. chim. ital.* 1874, 182). The air-dried plant was found to contain:

Water	Fats	Proteids	Carbohydrates	Mineral substance
26.15	2.55	3.77	61.26	6.27 = 100

The ash contains:

K ^a O	Na ^a O	CaO	MgO	Fe ^a O ^a	SO ^a	P ^a O ^a	SiO ^a *	(Cl, I, &c.)
4.07	8.61	36.89	14.50	7.62	3.05	2.54	20.86	1.84 = 99.98

* And other substances insoluble in hydrochloric acid.

POTASSIUM. According to Dolbear (*Chem. News*, xxvi. 33) and Kern (*Ber.* vi. 1208), this metal may be obtained by igniting its sulphide with iron-turnings.

Vapour-density.—Experiments by Dewar and Dittmar (*Proc. Roy. Soc.* xxi. 203) have shown that the vapour-density of potassium at the temperature of melting zinc does not exceed 45 [*H* = 1]. Consequently the molecule of potassium contains two atoms.

Reactions serving to distinguish Potassium from Sodium.—These metals may be distinguished from one another by their reaction with bromine. Sodium may be kept in bromine for months and even for years without perceptible alteration, and is but slightly corroded when heated therewith to 100°–200°, whereas potassium when thrown into bromine immediately takes fire, producing a violent explosion which often shatters the containing vessel. In like manner, sodium may be fused with iodine, without notable reaction, but potassium, when fused with iodine, explodes and flies to pieces in a jet of fire. Sodium immersed in aniline, even at the boiling heat, remains quite bright, while any crusts that may have formed upon its surface fall off, leaving it with the most splendid metallic lustre; potassium, on the other hand, reacts violently with aniline (Merz and Weith, *Ber.* vi. 1518).

Estimation of Potassium.—F. Mohr (*Zeitschr. anal. Chem.* 1873, 137) heats the precipitate of potassium chloroplatinate to fusion with twice its weight of sodium oxalate, and after washing and neutralisation with acetic acid, titrates with decinormal silver solution.

To avoid the troublesome employment of a weighed filter for collecting the precipitate of potassium chloroplatinate, Fresenius (*ibid.* 1877, 63) collects the precipitate in the ordinary way; transfers it when dry to a watch-glass; dissolves the small portion of the salt which adheres to the filter in a little hot water; evaporates the solution to dryness in a platinum capsule; then adds the rest of the salt; and dries the whole at 130°. It is absolutely necessary to test the potassium chloroplatinate as to its purity; when precipitated from solutions containing alkaline earths, it is sure to be impure. See also G. Krause (*Arch. Pharm.* [3], v. 407; *Jahresb. f. Chem.* 1874, 978).

Schloesing's method of estimating potassium by means of soluble perchlorates (vii. 1006) has been subjected to an experimental examination by Kraut, Ortmann, and Küsel (*Zeitschr. anal. Chem.* 1875, 152), who have arrived at the following

results. Instead of using ammonium perchlorates and nitrohydrochloric acid, it is preferable to treat the potassium salt under examination with an excess of pure distilled perchloric acid, and evaporate the mixture to dryness on the water-bath. The cooled residue is treated with alcohol of sp. gr. 0.835 to remove the free acid, then dissolved in hot water, the solution again evaporated on the water-bath, and the residue transferred by washing with alcohol of the same strength, to a filter previously weighed and moistened with alcohol. The presence of salts of sodium, barium, and other bases does not interfere with the result.

For the detection of small quantities of potassium in mixtures, A. Carnot (*Compt. rend.* lxxxiii. 290, 338) makes use of a mixture of 1 pt. *basic bismuth nitrate* and about 2 pts. crystallised *sodium thiosulphate*. A solution of this mixture colours solid potassium salts yellow, and forms with potassium solutions a yellow precipitate consisting of a thiosulphate of bismuth and potassium, $\text{Bi}(\text{S}^2\text{O}^3)^2 \cdot 3\text{K}^2\text{S}^2\text{O}^3 + 2\text{H}^2\text{O}$. The reaction is extremely delicate, and may be used for the quantitative estimation of potassium if in the state of nitrate or chloride; sulphates, if present, must be first converted into chlorides. To perform the analysis, the potassium salt is strongly concentrated, and mixed with $2\frac{1}{2}$ pts. *basic bismuth nitrate* (equiv. to 2 pts. bismuth), and 7 pts. crystallised *sodium thiosulphate* for every 1 pt. of potassium hydrate supposed to be present in the solution; the mixture is then quickly stirred, and 250 c.c. of strong alcohol poured upon it. After a quarter of an hour, the yellow precipitate is collected on a filter and carefully washed with alcohol. The quantity of potassium present may then be estimated by converting the bismuth in the precipitate into sulphide, weighing it in that form, and calculating the potassium from the formula above given.

In subsequent communications (*Compt. rend.* lxxxiv. 1504; lxxxv. 301) Carnot gives the following modification of the method for solutions containing sulphuric acid. The concentrated liquid is mixed with a solution of *calcium thiosulphate*, and a sufficient quantity of the bismuth solution; alcohol is added; and the resulting precipitate, a mixture of calcium sulphate and bismuth-potassium thiosulphate, is collected on a filter. On treating this precipitate with water, the bismuth-salt is dissolved, together with a small quantity of gypsum. The bismuth is then determined as above, and the potassium calculated therefrom.

The method of precipitation as bismuth-potassium thiosulphate serves admirably for the quantitative separation of potassium from many metals, *e.g.* sodium, lithium, ammonium, calcium, magnesium, aluminium, manganese, iron (as ferric salt), &c., inasmuch as, with the exception of the chlorides of barium, strontium, and those metals which are precipitated by hydrogen sulphide, no metallic chlorides give with bismuth salts and sodium thiosulphate a precipitate like that above mentioned.

P. Casamajor (*Chem. News*, xxxiv. 231, 242) estimates potassium volumetrically in the form of *acid tartrate*. The method is especially applicable to technical purposes. To separate the salt more effectually, the liquid is mixed with alcohol in such quantity as to form about 60 per cent. of the whole. If the potash is combined with strong acids, an excess of sodium acetate is added. The presence of sodium salts does not interfere with the attainment of accurate results. The acid tartrate may also, but less advantageously, be determined gravimetrically.

To separate potassium from a large excess of sodium salts, R. H. Loughridge mixes the nitrates of the two alkali-metals with *oxalic acid*, evaporates at 100° , whereby they are converted into acid oxalates, and treats the mixed salts with a small quantity of water, which dissolves the potassium oxalate, leaving the much less soluble sodium oxalate undissolved. The whole of the potassium salt is thus obtained in solution, together with only a small quantity of sodium salt, and the separation may then be completed by precipitating the potassium as chloroplatinate (*Amer. Chemist*, iii. 369).

Potassium Fluoride. This compound unites with *chromic anhydride*. On boiling a strong solution of potassium dichromate with hydrofluoric acid, octohedral and cubical crystals are obtained, having the composition $\text{KF} \cdot 2\text{CrO}^3$. This salt may be recrystallised from a small quantity of water, but is decomposed by a large excess. The crystals are efflorescent and attack glass. They are decomposed by sulphuric acid, with liberation of hydrofluoric and chromic acids. Treated with alkalis, they yield potassium fluoride and chromate (L. Varenne, *Compt. rend.* lxxxix. 358).

Iodide. G. Langbein (*Ber.* vii. 765) recommends the use of cuprous iodide, now largely imported from Peru, for the preparation of potassium iodide. The cuprous iodide is washed, suspended in water in the form of fine powder, and decomposed by hydrogen sulphide, and the resulting solution of hydriodic acid, freed from excess of hydrogen sulphide by addition of iodine, is neutralised with normal or acid carbonate of potassium. To prepare potassium iodide having a perfectly neutral reaction, T. B. Groves (*Pharm. J. Trans.* [3], iv. 669) dissolves the commercial salt, which

mostly has an alkaline reaction, in the exact quantity of water required, neutralises it with sulphuric acid, and throws down the potassium sulphate with alcohol. The decanted liquid, when evaporated, yields perfectly pure colourless crystals of potassium iodide.

A process for preparing potassium iodide free from iodate is given by G. Pellagri (*Ber.* viii. 1357), depending on the fact that the iodate in dilute solution is reduced by agitation with iron filings or zinc-powder (not by copper or tin) whilst the metal is directly oxidised. Agitation with iron filings in a warm solution produces complete reduction, without dissolution of the iron or transference of the iodine to the precipitate. If the solution is too concentrated, and a considerable quantity of ferric oxide has been formed, this oxide may exert an oxidising action on the potassium iodide. When an iron and a copper plate are immersed in a strong solution of potassium iodate, and connected externally by a wire, so as to form a galvanic couple, complete reduction takes place even at ordinary temperatures. Under those circumstances, only the iron is oxidised, and, the surface being small, the reduction takes several days to complete. No contamination of the product or loss of iodine takes place. Zinc-powder acts more energetically than iron filings, but for complete reduction a zinc-copper couple is necessary. *Potassium bromate* is completely reduced to bromide by an iron-copper couple; the *chlorate* very slowly and incompletely to chloride; but, by agitation with iron filings in a warm solution, this salt is quickly reduced. The formation of potassium iodate by the action of iodine on potash-solution is not prevented by the presence of suspended iron filings.

Polyiodides. A *tri-iodide*, KI^3 , is obtained, by slowly evaporating a saturated solution of iodine in potassium iodide over sulphuric acid, in shining, dark-blue, prismatic crystals, often 2 in. long. The crystals are very hygroscopic, and deliquesce completely after a short time to a dark-brown liquid; they dissolve also in alcohol. Their specific gravity, which is difficult to determine, on account of their great tendency to deliquesce, was found, on the average, to be 3.498 at 15°. The salt, when cautiously heated, melts at 45°; at a higher temperature it gives off iodine (1 mol.), and leaves ordinary potassium iodide (G. S. Johnson, *Chem. Soc. J.* xxxi. 249).

To determine whether the true formula of this salt is KI^3 , or a multiple thereof, Johnson (*ibid.* xxxiii. 183) has prepared polyiodides containing two or more different metals. When a solution of silver iodide and potassium iodide in the ratio of 1 mol. AgI to 1 mol. KI is mixed with iodine, a precipitate is formed, long before sufficient iodine has been added to form the compound $AgKI^2$, consisting of silver iodide, which may be redissolved by simply adding fresh quantities of potassium iodide. It is only when the iodides of silver and potassium and free iodine have been brought together in the proportion to form the compound AgK^2I^{12} that a clear solution is formed, which, on spontaneous evaporation, first deposits crystals of potassium-silver iodide, then of potassium tri-iodide, and finally crystals of a potassium-silver polyiodide having the composition $AgK^2I^{12}.KI + 5H^2O$. These crystals are mostly black and have a peculiar lustre; they are very deliquescent, but, nevertheless, effloresce over sulphuric acid. In attempting to prepare the corresponding potassium-thallium polyiodide, TlK^2I^{12} , Johnson obtained only the polyiodide discovered by Wilm (v. 751), which, in accordance with Wilm, he finds to be represented by the formula TKI^4 , and not by $Tl^2KI^2 + 3H^2O$, as stated by Rammelsberg (vii. 1151); Johnson is, however, of opinion that it contains 2 mols. H^2O . Lastly, Johnson has examined the precipitate formed on adding an iodised solution of potassium iodide to lead acetate, and finds it to be represented by the complex formula $Pb^2C^{26}H^{10}O^{28}K^6I^{17}$.

Hydride, K^2H . Fused potassium begins to absorb hydrogen at a temperature above 200°, the absorption becoming more rapid between 350° and 400°. The product obtained by keeping the metal in the gas for a long time is very brittle, has the aspect, lustre, and crystallo-granular structure of silver-amalgam, and indeed looks very much like a true alloy. It may be fused without alteration in hydrogen or in a vacuum. In contact with the air it immediately takes fire. When heated in a vacuum at 200° it begins to decompose, and from that temperature to 430° a regular dissociation takes place; in an atmosphere of hydrogen the decomposition takes place at 411°. The analysis of this compound gave 126 vols. H to 1 vol. K; the formula K^2H (which is of course only empirical) requiring 124.6 vols. H to 1 vol. K (Troost and Hautefeuille, *Ann. Chim. Phys.* [5], ii. 273).

Oxides (S. Lupton, *Chem. Soc. J.* xxx. 565). Potassium heated in air at about 65° for six hours is oxidised to a greenish powder mixed with small blue and yellow lumps. The blue lumps when separated were found to have the composition $K^2O^3 = 3K^2O + K^2O^2$. After the action had been continued for six hours more, the blue lumps gave numbers agreeing with the formula $K^4O^3 = K^2O + K^2O^2$. Similar blue lumps obtained with nitrogen monoxide as the oxidising agent, were found to consist of $K^2O^4 = 2K^2O + K^2O^2$. From these results it is probable that the blue oxide, which forms on a freshly-cut surface of potassium, is not a suboxide, as commonly

supposed, but a molecular compound of the monoxide and dioxide of potassium in various proportions, and that the grey oxide K^2O (theoretically improbable) described by Berzelius, must have contained metallic potassium. The yellow lumps, when likewise picked out, were found to have the composition of potassium dioxide. The green powder was found to contain a quantity of potassium greater than that required by the formula of that oxide, and appears to be a mixture of the dioxide with the blue oxides, but after fusion in a porcelain crucible it has exactly the composition of the dioxide K^2O^2 . When a platinum crucible lined with gold is used, the oxidation proceeds still further, oxides being formed which contain from 66 to 68 per cent. potassium. The dioxide is likewise obtained when potassium is heated for a considerable time in nitrogen monoxide. These results fully establish the existence of a dioxide of potassium, the occurrence of which in aqueous solution was pointed out by Harcourt in 1861 (iv. 706).

The following reactions of the green mixture are worthy of notice. When it is treated with hydrochloric and sulphurous acids, a certain quantity of sulphate is formed. With absolute alcohol it yields a yellow flocculent precipitate, which dissolves very slowly. Heated on a carbon boat in a stream of nitrogen, it assumes a yellow colour changing to orange-red, glows at the moment of fusion, and yields a speculum of metallic potassium, together with carbonate: $3K^2O^2 + C^2 = K^2 + 2K^2CO^2$. Heated with magnesia in a stream of nitrogen, it forms at first an orange-coloured viscid mass, which melts at a higher temperature, then suddenly gives off nitrogen, and is converted into a white mass—a reaction which appears to depend on the formation, in the first instance, of magnesium dioxide, which is then resolved at a higher temperature into magnesia and oxygen. When the brownish-yellow dioxide is exposed to moist air, it becomes continually lighter in colour, the lemon-yellow trioxide K^2O^3 being first formed, then the sulphur-yellow tetroxide K^2O^4 , which is again converted into trioxide, and finally into hydroxide. Attempts to prepare a definite oxide by heating potassium nitrate did not yield satisfactory results.

POTATO. *Solanum tuberosum*.—A series of investigations of the amounts of starch and dry substance in potatoes of various kinds has been made by L. Raab (*N. Jahrb. Pharm.* xxxvii. 204; xxxix. 15), showing that the proportion of starch varies from 8.8 to 26 per cent., and that of dry substance from 15.6 to 34 per cent.

Solanine in Potatoes.—According to O. Bach (*J. pr. Chem.* [2], vii. 248), solanine is found in sprouted potatoes only in the rind and at the roots of the sprouts. In the water, either fresh or salt, poured off from the boiled potatoes, the presence of solanine could be detected only by evaporating very large quantities.

Ash.—The ash of three sorts of potato has been analysed by J. B. Hannay (*Chem. News*, xxvii. 147). No. 1. Healthy potatoes from black dry soil gave 3.8 per cent. ash. No. 2. Diseased potatoes from the same soil, unfit for food, either for man or beast, gave 3.9 per cent. No. 3. Less diseased, from a loamy soil.

	No. 1.	No. 2.	No. 3.
<i>Soluble:</i>			
Potassium	36.77	37.86	43.11
Sodium	3.24	3.12	0.68
Magnesium	1.87	—	0.04
Carbonic anhydride	15.83	15.57	15.45
Phosphoric „	8.37	6.90	5.55
Sulphuric „	4.95	5.44	6.28
Chlorine	4.61	6.96	7.37
<i>Insoluble:</i>			
Silica	1.74	6.12	1.02
Ferric oxide and alumina	0.62	0.89	1.17
Calcium	3.70	2.80	2.92
Magnesium	0.88	0.60	0.02
Carbonic anhydride	2.90	1.45	1.34
Phosphoric „	3.70	3.06	6.20
Unburnt charcoal	1.98	—	—
Oxygen	9.64	9.03	9.23
	100.70	99.80	100.38

A. S. Wilson (*Chem. News*, xxviii. 91) found the ash of diseased potatoes to be composed as follows:

K	Na	Mg	Ca	P ² O ⁵	SO ²	CO ²	Cl	Fe ² O ³	SiO ²	O
44.51	0.25	2.36	1.12	14.48	5.57	15.80	1.37	0.53	2.89	11.22 = 100.10

The following table of the relations between the amount of starch in potatoes and their specific gravity has been drawn up by F. Heidepriem (*Landw. Vers.-St.* xx. 1) from the results of experiments made in 1875 by the Agricultural Society of Cöthen.

Relations between the amount of Starch in Potatoes and the Specific Gravity.

Weight of 5 kilograms under water	Starch per cent.	Dry substance per cent.	Weight of 5 kilograms under water	Starch per cent.	Dry substance per cent.
630	25.07	32.29	455	15.97	23.19
625	24.81	32.03	450	15.71	22.93
620	24.55	31.77	445	15.45	22.37
615	24.29	31.51	440	15.19	22.41
610	24.03	31.25	435	14.93	22.15
605	23.77	30.99	430	14.67	21.89
600	23.51	30.73	425	14.41	21.63
595	23.25	30.47	420	14.15	21.37
590	22.99	30.21	415	13.89	21.11
585	22.73	29.95	410	13.63	20.85
580	22.45	29.69	405	13.37	20.59
575	22.21	29.43	400	13.11	20.33
570	21.95	29.17	395	12.85	20.07
565	21.69	28.91	390	12.60	19.82
560	21.43	28.65	385	12.34	19.55
555	21.17	28.39	380	12.08	19.30
550	20.91	28.13	375	11.82	19.03
545	20.65	27.87	370	11.56	18.78
540	20.39	27.61	365	11.30	18.55
535	20.13	27.35	360	11.04	18.26
530	19.87	27.09	355	10.78	18.00
525	19.61	26.83	350	10.52	17.73
520	19.35	26.57	345	10.26	17.48
515	19.09	26.31	340	10.00	17.22
510	18.83	26.05	335	9.74	16.96
505	18.57	25.79	330	9.48	16.71
500	18.31	25.53	325	9.21	16.43
495	18.05	25.27	320	8.95	16.17
490	17.79	25.01	315	8.69	15.91
485	17.53	24.75	310	8.43	15.65
480	17.27	24.49	305	8.17	15.39
475	17.01	24.23	300	7.91	15.13
470	16.75	23.97	299	7.65	14.87
465	16.49	23.71	290	7.39	14.61
460	16.23	23.45	285	7.13	14.35

Similar determinations have been made by A. Marke (*Dingl. pol. J.* cccxv. 517), who found the specific gravity to vary between 1.108 and 1.120; the total dry substance between 28.36 and 31.36 per cent., and the starch between 20.61 and 23.52 per cent.

Effect of Cooking on the Nutritive Power of Potatoes.—P. Wagner u. K. Schafer (*Ber. v. Landw.-Versuchsst.*, Darmstadt, 1874) have endeavoured to determine what mode of cooking potatoes is attended with the greatest loss of nutritive salts. For this purpose, they boiled peeled and unpeeled potatoes for three-quarters of an hour in quantities of water just enough to cover them, and at the same time steamed samples of the same potatoes in a tin-plate sieve fixed in the boiler above the water. The following are the results:

	Ash	K ² O	P ² O ⁵
1 kg. unboiled unpeeled potatoes contained .	7.70 g.	4.30 g.	1.79 g.
1 kg. „ peeled „ „ .	7.45	3.75	1.53

	The boiled water poured off from 1 kg. potatoes contained in grams:			Hence the potatoes lost, in 100 parts of their original contents		
	Ash	K ² O	P ² O ⁵	Ash	K ² O	P ² O ⁵
1. Unpeeled potatoes boiled in water	0.28	0.10	0.02	3.64	2.32	1.12
2. Unpeeled potatoes steamed .	0.09	0.03	0.005	1.17	0.69	0.03
3. Peeled potatoes boiled in water .	2.15	1.25	0.35	28.86	33.33	22.87
4. Peeled potatoes steamed .	0.55	0.26	0.07	7.38	6.93	4.57

For unpeeled potatoes, therefore, the loss of nutritive salts in boiling and steaming is but small; but for peeled potatoes, steaming has decidedly the advantage over boiling.

PREDAZZITE. This name was originally given to a mineral from Predazzo, in South Tyrol, supposed to be a definite compound of calcite and brucite, MgH^2O^2 (iv. 714). Microscopical observation, however, shows that it is merely a mixture of these two minerals, the particles of which may be separately distinguished; moreover, Lemberg has shown that when a cut plate of predazzite is heated nearly to redness, and then immersed in solution of silver nitrate, the particles of brucite (converted by the heat into MgO) are blackened by separation of silver oxide, while those of calcite remain white (Rammelsberg, *Mineral-Chemie*, 2 Auflage, 1875, ii. 242).

The mineral from Predazzo having thus been shown to be a mixture, A. Cossa (*Gazz. chim. ital.* 1877, 393) proposes to transfer the name *Predazzite* to the rock of Monte Somma, also a mixture of calcite and brucite, which forms the matrix of pericase. Analyses of this rock gave:

CO^2	CaO	MgO	FeO	H^2O	Sp. gr.
36.21	43.56	12.81	0.12	5.23 = 97.93	2.857
39.45	45.02	11.28	0.32	4.37 = 100.44	to
40.28	45.73	9.22	0.41	3.97 = 99.61	2.903

PREHNITIC ACID, $\text{C}^2\text{H}^2(\text{CO}^2\text{H})^4$, is formed, by separation of 6 at. hydrogen and 2 mols. CO^2 , when hydromollitic acid, $\text{C}^2\text{H}^2(\text{CO}^2\text{H})^2$, is heated with strong sulphuric acid (vi. 809). Prehnitic anhydride, $\text{C}^2\text{H}^2(\text{CO}^2\text{H})^2\text{C}^2\text{O}^2$, is formed by the action of heat on prehnitic acid (vii. 785).

PRICITE. See CRYPTOMORPHITE (p. 589).

PROPANE, $\text{C}^3\text{H}^8 = \text{CH}^3.\text{CH}^2.\text{CH}^3$. This hydrocarbon is formed, together with several others of the paraffin series, by the action of superheated steam on the distillation-products of the fatty acids. The crude product is agitated with strong sulphuric acid, and the oil which floats on the surface of the acid is treated with sodium carbonate, dried, and rectified (Cahours a. Demarcay, *Compt. rend.* lxxx. 1568).

Chloro- and Bromo-propanes.

Dichloropropanes, or Propylene Dichlorides, $\text{C}^3\text{H}^4\text{Cl}^2$ (Roboul, *Ann. Chim. Phys.* [5], xiv. 453). *a*-Dichloropropane, $\text{CH}^3.\text{CCl}^2.\text{CH}^3$, is generally prepared by the action of phosphoric chloride on acetone, but may also be obtained by direct combination of HCl with allylene. It boils at 69° – 70° , is converted by alcoholic potash into the chloropropylene, $\text{CH}^2=\text{CCl}.\text{CH}^3$, boiling at 23° – 25° , and by silver benzoate into the di-benzoic compound, $\text{CH}^3.\text{C}(\text{C}^2\text{H}^3\text{O}^2)^2.\text{CH}^3$.

β -Dichloropropane, $\text{CH}^3.\text{CH}^2.\text{CHCl}^2$, is prepared by the action of phosphoric chloride on propaldehyde, but a considerable quantity of the chloropropylene, $\text{CH}^3.\text{CH}=\text{CHCl}$, is formed at the same time. Its boiling point is 85° – 87° , and its density 1.143 at 10° . With alcoholic potash it yields the chloropropylene just mentioned, which at a higher temperature (130°), under the influence of the same reagent, is converted into allylene, $\text{CH}^2.\text{C}=\text{CH}$. It yields no diacetyl compound when treated with potassium acetate.

γ -Dichloropropane, $\text{CH}^3.\text{CHCl}.\text{CH}^2\text{Cl}$.—The action of HCl on allyl chloride, $\text{CH}^2=\text{CH}.\text{CH}^2\text{Cl}$, does not yield, like that of HBr on the bromide, a mixture of the two chloro-compounds, but only the *γ* -dichloropropane. Allyl chloride is heated for eighteen hours at 100° , with very concentrated hydrochloric acid, and the upper layer of the product, which is of a violet-black colour, is separated and submitted to fractional distillation. The greater part of it consists of ordinary or *γ* -dichloropropane, boiling at 96° – 97° . The difference (22°) between the boiling points of the symmetrical and unsymmetrical dichloropropanes is the same as the difference between those of the corresponding dibromopropanes.

δ -Dichloropropane, or Trimethylene chloride, $\text{CH}^2\text{Cl}.\text{CH}^2.\text{CH}^2\text{Cl}$, may be obtained from the corresponding dibromide by heating it with mercuric chloride in sealed tubes at 180° for several hours, or by treating symmetrical propyl glycol with HCl . In the latter case, a monochlorhydrin of the glycol, $\text{CH}^2(\text{OH}).\text{CH}^2.\text{CH}^2\text{Cl}$, is formed at the same time. The two compounds are, however, easily separated, since the dichloropropane boils at 119° , and the monochlorhydrin at 162° . The density of the dichloropropane is 1.201 at 15° .

Dibromopropanes, or Propylene Dibromides. *a*-Dibromopropane, $\text{CH}^3.\text{CBr}^2.\text{CH}^3$.—It appears to be almost impossible to prepare this body by the action

of PBr_3 on acetone, but it can be easily prepared by the direct addition of HBr to allylene, or to α -bromopropylene. When hydrobromic acid of not less than 66°B . is added to allylene enclosed in a vessel over mercury, the absorption of the gas is complete in about four or six hours at 0° , and by replacing the gas as it is absorbed, very considerable quantities of the dibromide can be obtained. The product is, however, contaminated with a little α -bromopropylene, from which it can be readily separated by a few distillations.

The action of HBr on α -bromopropylene also gives a very pure product; but it is more convenient to work upon the mixture of propylenes given by ordinary dibromopropane in the manner which will be described under β -bromopropylene (p. 1679). The density of α -dibromopropane at 10° is 1.875, and its boiling point 114° – 114.5° under 740 mm.

β -Dibromopropane, $\text{CH}_3\text{CH}_2\text{CHBr}_2$.—Although the existence of this bromide can be shown independently of theoretical considerations, it has never been satisfactorily isolated. The action of PBr_3 on propyl aldehyde closely resembles the corresponding action on acetone; torrents of HBr are evolved from the commencement of the operation, but as soon as distillation is proceeded with, the liquid turns black, evolves more HBr , and leaves finally an abundant carbonaceous residue. From the distillate, after the removal of phosphorus oxybromide, a little β -bromopropylene can be separated, but no β -dibromopropane can be obtained. The operation is not more successful when the oxybromide is removed by means of water, without previous distillation.

By combining HBr with the bromopropylene, $\text{CH}_3\text{CH}=\text{CHBr}$, in the cold, the two dibromopropanes are simultaneously produced. Fractional distillation, however, fails to separate them, on account of the proximity of their boiling points. On submitting the washed and dried liquid to distillation, the boiling point quickly rises to 135° , and the whole passes over between 135° and 143° , the greater portion distilling between 139° and 140° . The boiling point of the β -compound should be 131° – 133° , while that of the ordinary or γ -dibromopropane, $\text{CH}_3\text{CHBrCH}_2\text{Br}$, is 143° (vii. 1017). The same result is obtained if the combination of HBr with the bromopropylene takes place at 100° .

δ -Dibromopropane, or Trimethylene bromide, $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$.—The action of HBr on allyl bromide forms simultaneously two isomerides, the normal or δ -dibromopropane and the ordinary or γ -dibromopropane. The relative proportion of the two bromides varies with the concentration of the acid, with the temperature, and with the duration of the action. The best method of operating is as follows: 1 vol. of allyl bromide and $3\frac{1}{2}$ vols. of fuming hydrobromic acid are heated under pressure at 100° for fifteen to twenty minutes, and the dark-coloured oily product subsequently washed and distilled. A good deal of unaltered allyl bromide passes over first, and then the thermometer rapidly rises to 140° – 145° . The distillate is collected from this point up to 175° . On submitting this portion to repeated fractional distillation, the δ -dibromopropane can be easily separated, boiling at 164° – 165° , the yield being a little more than one-half the allyl bromide used. If the solution of hydrobromic acid is not saturated, or if the time of heating be prolonged, a largely increased yield of ordinary dibromide is obtained at the expense of the normal or δ -compound; even with a strongly fuming acid, it is not advisable to heat the mixture longer than twenty minutes, for no increased yield of the desired product is obtained. Its density is 1.9839 at 13.5° . It is much more susceptible of double decomposition than the ordinary dibromide, forming with great facility the compound ethers of the corresponding glycol.

According to Erlenmeyer (*Liebig's Annalen*, cxcvii. 184), the conditions most favourable to the formation of trimethylene bromide are as follows: (1) Dry hydrobromic acid in large excess should be kept in contact with the allyl bromide until the reaction is ended, and the temperature should be maintained at 30° – 40° ; (2) the more diluted the hydrobromic acid becomes, either by water or by trimethylene bromide, the larger is the quantity of ordinary propylene dibromide formed. When the required dilution has been produced by the formation of trimethylene bromide, the remaining hydrobromic acid unites with allyl bromide to form ordinary propylene bromide, this reaction taking place more quickly at high than at low temperatures; (3) the formation of trimethylene bromide takes place first at temperatures from 0° – 30° , and, in the case of sufficiently concentrated solutions, even at temperatures above 100° . The formation of ordinary propylene bromide commences in dilute hydrobromic acid solutions at low rather than at high temperatures.

Chlorobromopropanes, or Propylene Chlorobromides. Five chlorobromopropanes ought theoretically to exist, viz. α , β , and δ , analogous to the chlorides and bromides α , β , and δ , and two others, γ and γ' , analogous to the chloride γ .

α-Chlorobromopropane, $\text{CH}^3\text{.CClBr.CH}^3$, is very easily obtained by the action in the cold of excess of concentrated hydrobromic acid on *α*-chloropropylene. The γ -modification, $\text{CH}^3\text{.CCl.CH}^2\text{Br}$, is not produced in the cold, but only on heating. The *α*-compound boils at $43^\circ\text{--}93\cdot5^\circ$, and its density is $1\cdot474$ at 21° .

Bromiodopropane may be prepared in a similar manner by the action of HI on *α*-bromopropylene. On distillation nearly the whole product passes over at 147° , slightly coloured by free iodine. Its density is $2\cdot2$ at 11° .

β-Chlorobromopropane, $\text{CH}^3\text{.CH}^2\text{.CHClBr}$, results from the addition of HBr to *β*-chloropropylene without application of heat. It is generally accompanied by a small quantity of the γ -compound, $\text{CH}^3\text{.CHBr.CH}^2\text{Cl}$, but the latter is easily separated by distillation. Its density is $1\cdot59$ at 20° , and its boiling point $110^\circ\text{--}112^\circ$.

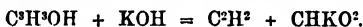
γ-Chlorobromopropanes, $\text{CH}^3\text{.CHCl.CH}^2\text{Br}$ and γ' $\text{CH}^3\text{.CHBr.CH}^2\text{Cl}$.—By maintaining for some hours at the boiling point a mixture of ordinary dibromopropane and mercuric chloride in an apparatus fitted with an inverted condenser, Friedel a. Silva obtained a chlorobromide boiling at $119^\circ\text{--}121^\circ$, which they considered to be the compound $\text{CH}^3\text{.CHCl.CH}^2\text{Br}$, because when decomposed with alcoholic potash it yielded *α*-chloropropane boiling at $25^\circ\text{--}30^\circ$. Reboul, however, points out that the chlorobromide made in this manner is in reality a mixture of the two isomerides.

δ-Chlorobromopropane, $\text{CH}^2\text{Cl.CH}^2\text{CH}^2\text{Br}$, is prepared by heating allyl chloride for seven or eight hours at 100° in a closed vessel, with a concentrated solution of hydrobromic acid, then washing, drying, and fractionating. When quite free from allyl chloride, it distils at $140^\circ\text{--}142^\circ$, and has a density of $1\cdot63$ at 8° ; it is, however, very difficult to free it entirely from a trace of the γ -compound, $\text{CH}^3\text{.CHBr.CH}^2\text{Cl}$, and of *δ*-dibromopropane, which are formed at the same time.

By the action of sodium on the isomeric bromopropanes, one and the same propylene is always formed, namely, $\text{CH}^3\text{.CH=CH}^2$.

When the two chlorine or bromine atoms in the dichloro- and dibromopropanes are attached to the same carbon-atoms, they cannot be replaced by acid radicles; when the propane-derivatives thus constituted are treated with silver acetate, they lose HCl or HBr and are converted into monochloro- or monobromopropylene. In the case of *α*-dibromopropane, $\text{CH}^3\text{.CBr}^2\text{.CH}^3$, it is possible to obtain a dibenzoyl-compound, but water resolves it into acetone and benzoic acid.

PROPARGYL-COMPOUNDS (vii. 1006). The following additional observations on these compounds have been published by L. Henry (*Ber.* viii. 398). *Propargyl Alcohol* is wholly resolved by the action of potassium hydroxide into acetylene and formic acid:



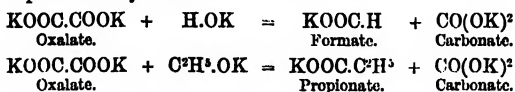
Propargyl chloride, $\text{C}^3\text{H}^3\text{Cl}$, produced by the action of phosphorus trichloride on the alcohol, is a mobile liquid, having a disagreeable odour, insoluble in water, boiling at 65° , and having a density of $1\cdot0454$ at 5° .

The *iodide*, $\text{C}^3\text{H}^3\text{I}$, formed from the alcohol by the action of iodine and amorphous phosphorus, crystallises in small needles, melts at $48^\circ\text{--}49^\circ$, dissolves slightly in water, abundantly in alcohol and ether, and is decomposed by distillation.

PROPARGYLENE. See ALLYLENE (p. 63).

PROPIONIC ACID, $\text{C}^3\text{H}^3\text{O}^2 = \text{CH}^3\text{.CH}^2\text{.COOH}$. In preparing this acid from ethyl cyanide (iv. 730), Th. D. Barry (*Inaug. Diss.* Halle, 1874) finds that a better product is obtained by boiling the ethyl cyanide with alcoholic potash than with dilute sulphuric acid. From 2 kg. potassium ethylsulphate and 2 kg. potassium cyanide he obtained 471 g. crude ethyl cyanide yielding 390 g. potassium propionate.

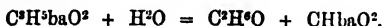
Propionic acid is also formed by heating potassium oxalate with dry sodium ethylate, the reaction being analogous to that by which formic acid is obtained from oxalic acid and potassium hydroxide:



Oily products distil over, and on lixiviating the residue with water, supersaturating it with sulphuric acid, and distilling, a strongly acid distillate is obtained, containing formic and propionic acids (J. van 't Hoff, *Ber.* vi. 1107).

The supposed formation of a propionate by the action of carbon monoxide on a metallic ethylate has been already noted (vii. 1009). According to Berthelot, however (*Bull. Soc. Chim.* [2], xix. 160), the barium-compound obtained by passing carbon monoxide into a solution of barium alcoholate in absolute alcohol, though identical in composition with barium propionate, $\text{C}^3\text{H}^3\text{baO}^2$ [$\text{ba} = 68\cdot7$], differs from that salt in

being soluble in alcohol and in being decomposed by water, with formation of ethyl alcohol and barium formate :

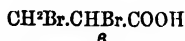
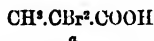


Berthelot therefore regards this salt as isomeric with barium propionate, and designates it as *ethylformate*. But ethyl-formic acid, $\text{C}^2\text{H}^3\text{COOH}$, as is well known, is nothing else than propionic acid, and according to the generally received views of the constitution of acids, no isomeride of propionic acid of the general type $\text{C}^n\text{H}^{2n+1}\text{COOH}$ is possible. Kolbe therefore regards Berthelot's salt as *formylated barium ethylate*, $\text{CH}^3\text{CH}(\text{CHO})\text{Oba}$ (*J. pr. Chem.* [2], viii. 27).

Propionic acid, heated in a sealed tube with iodine trichloride, yields perchloroethane, together with CO^2 and HCl , which escape on opening the tube (F. Krafft, *Ber.* ix. 1085). The reaction may perhaps be represented by the equation :



Bromopropionic Acids. The two dibromopropionic acids, represented by the formula



have been already described (vii. 1010-1012); also the two bromacrylic acids, $\text{CH}^2=\text{CB}r-\text{COH}$ and $\text{CHBr}=\text{CH}-\text{COOH}$, obtained from them by the action of boiling alcoholic potash (viii. 44).

Dichloropropionic Acids, $\text{C}^2\text{H}^3\text{Cl}^2\text{COOH}$. Two of these acids are known, analogous in constitution to the dibromopropionic acids.

The α -acid, $\text{CH}^3\text{Cl}^2\text{COOH}$, which Klimenko obtained by the action of alcohol on the chloride formed by treating pyroracemic acid, $\text{CH}^3\text{CO}\cdot\text{COOH}$, with phosphorus pentachloride (vii. 1012), is also produced by the action of strong hydrochloric or moderately strong sulphuric acid on dichloropropionitril, $\text{CH}^3\text{Cl}^2\text{CN}$ (iv. 736). The easiest way of preparing it is to heat 1 pt. of the nitril with 2 or 3 pts. of a mixture of sulphuric acid and water in equal volumes, in a reflux apparatus at about 20° . As soon as the layer of oil floating on the surface of the acid ceases to boil, it must be pipetted off and rectified with a thermometer in the liquid. Stronger acid or a larger quantity gives rise to the formation of brown decomposition-products (Beckurts a. Otto, *Ber.* ix. 1876).

α -Dichloropropionic acid boils without decomposition between 185° and 190° , and does not solidify at -8° . It volatilises with vapour of water. Its salts, excepting the silver salt, are permanent in the dry state at ordinary temperatures, but at higher temperatures, or when their solutions are heated (especially in contact with excess of base), they decompose, with separation of metallic chlorides. Most of them dissolve readily in water and in alcohol.

The *potassium salt*, $\text{C}^2\text{H}^3\text{Cl}^2\text{KO}^2 + 6\text{H}^2\text{O}$, forms shining needles or tufts, decomposing at 60° - 70° ; the *ammonium salt*, $\text{C}^2\text{H}^3\text{Cl}^2(\text{NH}^4)\text{O}^2$, thin, white, fatty laminae; the *silver salt*, $\text{C}^2\text{H}^3\text{Cl}^2\text{AgO}^2$, small white needles, soluble with difficulty in water; decomposed at ordinary temperatures; the *calcium salt*, $(\text{C}^2\text{H}^3\text{Cl}^2\text{O}^2)^2\text{Ca} + 3\text{H}^2\text{O}$, white, cheaf-like needles, of glassy or silky aspect; decomposed at 120° ; the *barium salt*, $(\text{C}^2\text{H}^3\text{Cl}^2\text{O}^2)^2\text{Ba} + \text{H}^2\text{O}$, glassy, rhombic laminae, which lose their water of crystallisation at 80° and become opaque; the *zinc salt*, $(\text{C}^2\text{H}^3\text{Cl}^2\text{O}^2)^2\text{Zn} + \text{H}^2\text{O}$, transparent needles resembling the sulphate; they lose their water of crystallisation at 60° , and are decomposed at 80° .

The ethers of α -dichloropropionic acid are easily prepared by the action of hydrochloric acid on the solution of the acid in the corresponding alcohol. The *methyl ether* is a colourless liquid having a fruity odour, and boiling at 143° - 144° (uncorr.) The *ethyl ether*, identical with the ether formed from α -dichloropropionitril and alcohol in presence of sulphuric acid, boils at 156° - 157° . The *allyl ether* is a faint yellow liquid, which is decomposed on distillation, with separation of hydrochloric acid. It has a fruit-like smell, and boils at 176° - 178° . The *isobutyl ether* resembles the foregoing, is not completely decomposed at 183° - 185° ; has a pleasant pine-apple odour, Starting from the methyl ether, the boiling points of these ethers rise by intervals of about 10° .

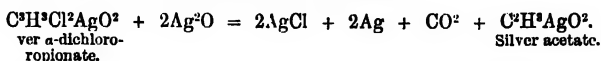
Behaviour of α -Dichloropropionic Acid to Nascent Hydrogen.—By the action of zinc and dilute sulphuric acid at ordinary temperatures, the acid is converted into propionic acid. The ethylic ether of α -dichloropropionic acid is also converted by similar treatment into the ethylic ether of propionic acid.

Conversion of α -Dichloropropionic Acid into Merochloracrylic Acid.—The aqueous solution of the silver salt of α -dichloropropionic acid becomes turbid at ordinary temperatures, and gradually deposits the whole of the silver as chloride; the change

is completed in a few minutes by boiling. The filtrate from the silver chloride contains an acid of the composition of monochloracrylic acid. It may be formed thus: $C^3H^3Cl^2AgO^2 = C^3H^3ClO^2 + AgCl$. The dry silver salt, even in closed vessels, suffers the same change at ordinary temperatures.

The potassium salt of monochloracrylic acid may also be obtained by heating an alcoholic solution of α -dichloropropionic acid (1 mol.) with a solution of potassium hydrate (2 to 3 mols.) This acid is not identical with the β -monochloracrylic acid of Werigo and Werner, but corresponds with the α -monobromacrylic acid of Philipp and Tollens.

Conversion of α -Dichloropropionic Acid into Acetic and Carbacetoxylic Acids.—When an aqueous solution of α -dichloropropionic acid is heated with freshly precipitated silver oxide, the following change takes place:



By treating an aqueous solution of α -dichloropropionic acid with silver carbonate, a salt is obtained in small brown needles which is probably the silver salt of carbacetoxylic acid (Beckurts a. Otto, *loc. cit.*)

Conversion of α -Dichloropropionic acid into Chloracrylic and Pyroracemic acids.—An aqueous solution of the silver salt of this acid is converted by boiling for a few minutes into a solution of monochloracrylic acid, with deposition of silver chloride: $C^3H^3Cl^2AgO^2 = AgCl + C^3H^3ClO^2$; and on heating the latter solution for some hours with oxide or better with carbonate of silver, the silver salt first formed is decomposed, and pyroracemic acid, $C^3H^3O^3$, is formed, according to the equation $C^3H^3ClAgO^2 + H^2O = AgCl + C^3H^3O^3$. These two reactions may be effected in one operation by simply heating a solution of α -dichloropropionic acid with an equal number of molecules of silver carbonate, till silver chloride is no longer formed, the following reaction then taking place:



(Beckurts a. Otto, *Ber.* x. 264).

α -Dichloropropionitril, $CH^3.CCl^2.CN$.—This compound exists in two physical modifications, one liquid and the other solid (iv. 736). The latter is regarded by Beckurts a. Otto as a polymeric modification of the former, inasmuch as when boiled with dilute sulphuric acid it reacts in the same manner, yielding α -dichloropropionic acid. Heated in a sealed tube with alcoholic ammonia, it is converted into α -dichloropropionamide, $CH^3.Cl^2.CONH^2$ (m. p. 115° – 116°). The solid modification is produced in greatest abundance when the action of chlorine on propionitril takes place at comparatively low temperatures; also, though in small quantity only, and accompanied by various brown amorphous products, when the liquid modification is boiled for some time in a reflux apparatus with potassium, sodium, or sodium-amalgam. In this reaction metallic chlorides and cyanides are also formed. The liquid modification is also converted into the solid when kept in imperfectly closed vessels, considerable quantities of hydrochloric acid being set free at the same time. The solid modification is perhaps a derivative of cyanethine (ii. 189) (Beckurts a. Otto, *Ber.* ix. 1593; x. 263, 2040).

β -Dichloropropionic acid, $CH^2Cl.CHCl.COOH$.—Werigo a. Okulitsch, by treating glyceric chloranhydride with alcohol, obtained a product which they regarded as the ethylic ether of β -dichloropropionic acid (vii. 563). Subsequent experiments by Werigo a. Melikoff (*Ber.* x. 1499), however, have shown that this product when saponified does not yield β -dichloropropionic acid. But, if the glyceric chloranhydride be first converted by boiling with potash into chloracrylic acid, $CHCl=CH-CO^2H$, and the latter be heated with hydrochloric acid, it takes up HCl and is converted into β -dichloropropionic acid, melting at 50° , and yielding an ethylic ether which boils at 183° – 184° . The β -acid is, however, more easily obtained, together with chlorolactic acid, by heating glyceric acid in sealed tubes for three days with hydrochloric acid saturated at 0° (W. and M. *Ber.* xii. 178). L. Henry (*Ber.* vii. 414; *Bull. Soc. Chim.* [2], xxx. 161) has also obtained the β -acid by the action of fuming nitric acid at the heat of the water-bath on unsymmetrical dichlorhydrin, $CH^2Cl.CHCl.CH^2OH$ (p. 876). It may be extracted from the product by ether, in which it dissolves readily, as also in alcohol and water; crystallises in needles; melts at 50° ; and yields an ethylic ether which boils at 180° . The identity of the dichloropropionic acid from glyceric acid with that obtained from unsymmetrical dichlorhydrin is further shown by the fact that both yield the same β -chloracrylic acid melting at 64° – 65° (Werigo a. Melikoff).

Cyanopropionic Acid, $C^1H^2NO^2 = C^2H^1(CN).COOH$ (Wanklyn a. Cooper, *Phil. Mag.* [5], vii. 356). This acid is formed, together with others, when wool (1 pt.) dissolved in water containing potassium hydroxide (3 pts.) is oxidised by 2 pts. of potassium permanganate. It is obtained pure by converting it into a barium salt and decomposing the latter with sulphuric acid.

Cyanopropionic acid in the free state is an amorphous solid, brittle at ordinary temperatures, but softening at 100° . In mass, it has a pale brownish-yellow or straw colour; in powder it is almost white. It is very soluble in water and in strong alcohol; has a strongly acid taste and reaction; decomposes carbonates, and dissolves magnesium in the cold. It is oxidised by potassium dichromate and by permanganate. Heated at 140° , it gives off all its water; at higher temperatures, it is decomposed, evolving ethyl cyanide, and forming a brown mass, soluble in potash. The potassium salt, heated with twice its weight of potassium hydroxide, is completely decomposed, giving off ethylamine and leaving potassium oxalate:



Most of the metallic cyanopropionates are soluble in water, and contain water of crystallisation. *Barium cyanopropionate*, $Ba(C^1H^2NO^2)^2.3H^2O$, is a white powder, very soluble in water, but sparingly soluble in alcohol. It loses 1 mol. of water at 160° - 170° . There is also a basic salt, $[Ba(C^1H^2NO^2)^2.3H^2O]^2.BaH^2O^2$. The *silver salt*, $2C^1H^2AgNO^2.3H^2O$, is nearly insoluble in water; the dry salt quickly absorbs 2 per cent. of water. There is also a basic salt, $2C^1H^2AgNO^2.AgHO.H^2O$, obtained by adding silver nitrate to the basic barium salt. The *lead salt*, $Pb(C^1H^2NO^2)^2.H^2O$, is a white powder, nearly insoluble in water. The *magnesium salt*, $Mg(C^1H^2NO^2)^2.3H^2O$, is extremely soluble in water, drying up first to a jelly, and finally to a brittle mass, yielding a white powder. The *potassium salt*, $C^1H^2KCO^2.H^2O$, forms a straw-coloured transparent solid. Dried at 100° , it contains 5 mols. of water; at 190° , only 1; deposited from strong alcohol and dried at 100° , it contains $4H^2O$. It is very soluble in water and in 40 per cent. alcohol, sparingly in strong alcohol. The *calcium salt*, $Ca(C^1H^2NO^2)^2.4H^2O$ (dried at 100°), is very soluble in water, and is precipitated from its aqueous solution by alcohol of 84 per cent. It loses about 4 per cent. (rather less than $\frac{1}{2}$ mol.) of water at 200° .

PROPIONYL-PROPIONATE, ETHYLIC, $CH^3.CH^2.CO.CH^2.CH^2.COO.C^2H^5$.

This ether is formed by digesting ethyl propionate in a Frankland's apparatus (i. 521) with sodium. About $\frac{2}{3}$ of an equivalent of the metal is thereby dissolved, and on adding acetic acid to the product, ethyl propionylpropionate is separated as a liquid resembling ethyl acetate, but having a still more fragrant odour. Sp. gr. 0.9048 at 0° . B. p. 180° - 205° . It gives no colour-reaction with ferric chloride, and does not unite with mercuric oxide, whereas ethyl acetoacetate unites with that oxide, forming a white insoluble mass (Oppenheim a. Hellon, *Ber.* x. 699).

PROPIOPHENONE, $C^6H^5.CO.C^2H^5$. See KETONES (p. 1152).

PROPYL ALCOHOLS AND ETHERS. *Normal Propyl Alcohol*, $CH^3.CH^2.CH^2.OH$.—On the formation of this compound from allyl alcohol by the action of nascent hydrogen (zinc and sulphuric acid), see ALLYL ALCOHOL (p. 59). It is found, together with butyl alcohol, in the sour waters of the wheat-starch manufacture, and in the volatile products of the lactic and butyric fermentation of glucose (Bouchardat, *Compt. rend.* lxxviii. 1145). Linnemann, by heating the nitrite of normal propylamine, obtained isopropyl alcohol (vii. 1015). According to Meyer a. Forster, however (*Ber.* ix. 535), the product thus obtained is a mixture 42 per cent. normal and 58 per cent. isopropyl alcohol.

According to Klimenko (*Bull. Soc. Chim.* [2], xxv. 294), propyl alcohol is converted by oxidation with nitric acid into propyl acetate, oxalic acid, and carbon dioxide.

Bromine acts on propyl alcohol in the same manner as on ethyl alcohol (p. 744), producing the propyl-alcoholate of propyl-bromal, $C^3H^5Br^2O.C^3H^5O$, which is a slightly yellowish liquid (Hardy).

On the reaction of propyl alcohol with *urea*, see CARBAMATES (p. 385).

Propyl Chlorocarbonate, $Cl.CO.OC^3H^7$, is formed by the action of phosgene gas on normal propyl alcohol. The products, after washing with water and drying over calcium chloride, boil between 90° and 160° , the greater part distilling over at 120° - 130° , and consisting of nearly pure chlorocarbonate. This ether is a liquid, heavier than water, giving off a pungent vapour which strongly attacks the eyes, and burning with a green flame. It is easily decomposed by distillation, and cannot therefore be purified by fractionation (H. Roemer, *Ber.* vi. 1101). *Propyl Carbonate*, $CO(OC^3H^7)^2$, is formed by dropping an ethereal solution of the chlorocarbonate on sodium propyl-

ate (Roemer); also by the action of sodium on the oxalate (Cahours, *Compt. rend.* lxxvii. 749). It is a colourless, mobile, fragrant liquid, burning with a blue flame, and boiling at 160° – 165° (Roemer); 156° – 160° (Cahours). Sp. gr. 0.968° at 22° (Cahours). *Propyl Carbamate*, $\text{NH}^{\cdot}\text{CO.OC}^{\text{H}}^{\cdot}$, formed by the action of aqueous ammonia on the chlorocarbonate, crystallises in large colourless prisms, easily soluble in alcohol and ether, less soluble in water, melting at 50° ; comp. Cahours (p. 385). *Propyl Phenylcarbamate*, $\text{NH}(\text{C}^{\text{H}}^{\cdot})^3.\text{CO.OC}^{\text{H}}^{\cdot}$, formed in like manner with an ethereal solution of aniline, crystallises in slender needles, easily soluble in alcohol, less soluble in water, melting at 57° – 59° (Roemer). On *Ethylidene-Propylcarbonate*, $\text{CH}^{\cdot}.\text{CH}(\text{NH.CO.OC}^{\text{H}}^{\cdot})^2$, see CARBAMATES (p. 386).

Propyl Nitrite, $\text{C}^{\text{H}}^{\cdot}.\text{O.NO}$, formed by passing nitrogen trioxide into propyl alcohol, is a fragrant liquid, having a specific gravity of 0.935 at 21° , and boiling between 43° and 46° . On its isomeride, *nitropropane*, see p. 1491. The *oxalate*, $\text{C}^{\text{H}}^{\cdot}.\text{O.CO.CO.C}^{\text{H}}^{\cdot}.\text{O}$, is prepared by distilling anhydrous propyl alcohol with dry oxalic acid, either alone or mixed with $\frac{1}{2}$ pt. sulphuric acid. The distillate, on addition of water, separates into two layers, the upper of which, when washed, dried, and rectified, yields propyl oxalate as a liquid having an aromatic odour, a specific gravity of 1.018 at 22° , and boiling between 209° and 211° . Ammonia converts it into crystalline propyloxamate, $\text{C}^{\text{H}}^{\cdot}.\text{O.CO.CO.NH}^2$, which is decomposed by water, with reproduction of propyl alcohol and oxalic acid. The *salicylate*, $\text{C}^{\text{H}}^{\cdot}(\text{OH}).\text{COOC}^{\text{H}}^{\cdot}$, prepared from propyl alcohol, salicylic acid, and strong sulphuric acid, in the proportions $2 : 2 : 1$, forms, after washing, drying, and rectification, a colourless fragrant liquid, having a specific gravity of 1.021 at 21° , and boiling between 238° and 240° . It is slightly soluble in water, and dissolves in all proportions in alcohol and ether. It forms well-crystallised chloro- and bromo-derivatives, is converted by fuming nitric acid at ordinary temperatures into a nitro-derivative, and decomposed at the boiling heat with formation of picric acid. With ammonia it forms salicylamide. *Propyl Phenate*, $\text{C}^{\text{H}}^{\cdot}(\text{C}^{\text{H}}^{\cdot})^2\text{O}$, is formed, together with barium carbonate, by distilling propyl salicylate with baryta; more readily, however, by heating propyl iodide with an alcoholic solution of potassium phenate in a sealed tube at 100° – 110° . It is a colourless liquid, having a pleasant odour, a specific gravity of 0.968 at 20° , and boiling at 190° – 191° . It is violently attacked by strong nitric acid, and forms with bromine a crystalline substitution-product (Cahours, *Compt. rend.* lxxvii. 749).

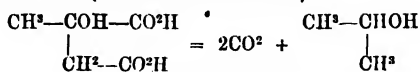
Propyl Sulphide, $(\text{C}^{\text{H}}^{\cdot})^2\text{S}$, obtained by heating potassium monosulphide with propyl chloride or iodide in alcoholic solution, boils at 130° – 135° , and has a density of 0.814 at 17° (Cahours, vii. 1014).

Metallic compounds of Propyl.—The compounds of propyl with *aluminium*, *glucinum*, *mercury*, *tin*, and *zinc*, discovered by Cahours, have been already described (vii. 1014).

When propyl iodide is heated with *arsenic* for twenty-four to thirty hours at 175° – 185° , a brown-red liquid is formed, which solidifies at low temperatures to reddish-brown crystals of the compound $\text{AsI}^{\cdot}.\text{As}(\text{C}^{\text{H}}^{\cdot})^3\text{I}$. Strong potash-ley decomposes this compound, with separation of an oil, and after the excess of potash has been saturated with carbonic acid, absolute alcohol extracts from the product *tetrapropyl-arsonium iodide*, which crystallises in colourless prisms. Iodine dissolves in its warm solution, forming a *polyiodide*, which separates on cooling in blackish-brown crystals having a metallic lustre. On distilling the above-mentioned double compound with caustic potash, tripropyl-arsine, $\text{As}(\text{C}^{\text{H}}^{\cdot})^3$, is obtained as a liquid which has an extremely offensive odour and unites directly with alcoholic iodides.

Zinc arsenide acts on propyl iodide at 175° – 180° , forming prismatic crystals of the compound $\text{ZnI}^{\cdot}.2\text{As}(\text{C}^{\text{H}}^{\cdot})^3\text{I}$, which is decomposed by strong potash-ley in the same manner as the double arsenic compound. The arsenides of potassium and sodium act very violently on propyl iodide, forming, together with *tetrapropyl-arsonium iodide*, a very offensive-smelling liquid, probably containing *di-* and *tripropyl-arsine* (Cahours, *Compt. rend.* lxxvi. 1383).

Iso- or Pseudopropyl Alcohol, $\text{CH}^{\cdot}.\text{CHOH}.\text{CH}^{\cdot}$.—This alcohol is formed: *a.* By the action of heat on propylamine nitrite (vii. 1015). *β.* Together with pinacene, by the action of sodium on acetone in contact with a strong solution of potassium carbonate (p. 1529). *γ.* Together with carbon dioxide, by dry distillation of hydroxypyrotartaric acid (see PYROTARTARIC ACID):



Flavitzky (*Liebig's Annalen*, clxxv. 380) prepares isopropyl alcohol by decomposing

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the corresponding iodide with water and lead oxide. Niederist (*ibid.* clxxxvi. 391) heats the iodide (20 to 25 grams) with 20 times its weight of water in a closed champagne bottle for forty hours.

Isopropyl-compounds are easily formed from haloid propylene-compounds. Propylene-glycol is converted by hydriodic acid into isopropyl iodide, and the oxide and oxychloride of propylene; by nascent hydrogen into isopropyl alcohol (Linnemann, *Lieb. Ann.* clxi. 45).

The following table exhibits the boiling points and densities of normal propyl iodide and isopropyl iodide at those temperatures at which their vapour-tensions are equal (F. D. Brown, *Proc. Roy. Soc.* xxvi. 238).

Vapour-tension in millimeters	Boiling point of normal propyl iodide	Boiling point of isopropyl iodide	Density of normal propyl iodide	Density of isopropyl iodide	Difference of densities
200	62.37°	50.50°	1.66704	1.64590	0.02114
300	73.51	61.33	1.64493	1.62359	0.02134
400	81.95	69.70	1.62808	1.60646	0.02162
500	88.84	76.44	1.61446	1.59246	0.02200
600	94.70	82.11	1.60250	1.58068	0.02182
700	99.83	87.13	1.59221	1.57035	0.02186
760	102.63	89.86	1.58670	1.56497	0.02196

PROPYL-ACETIC ACIDS, $(C^3H^7)CH^2.COOH$. See PENTOLIC ACIDS (p. 1500). According to N. Ley (*Ber.* x. 230), isopropyl-hydroxyacetic acid is resolved by oxidation into carbon dioxide, isopropyl aldehyde, and isobutyric acid.

PROPYL-(ISO)-ACETYLENE, $C^3H^8 = (CH^3)^2CH.C \equiv CH$, is obtained by the action of alcoholic potash on isopropylethylene dibromide, $(CH^3)^2CH.CHBr.CH^2Br$. It boils at 35° (Eltékoff, see PENTYLENES, p. 1503).

PROPYLAMINES, $C^3H^7NH^2$. Propylamine may be prepared by fermenting the digestive apparatus of cows, calves, sheep, or oxen for thirty-two to thirty-six hours at 59°–64.5° Fahr. with four or five times its weight of water and $\frac{1}{15}$ of potassium or sodium carbonate, then adding caustic soda, distilling off $\frac{1}{4}$ of the volume of liquid, converting the base therein contained into hydrochloride, distilling it with soda, and collecting the evolved vapours in water (E. Perret, *Pharm. J. Trans.* [3], iii. 884).

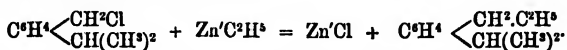
Isopropylamine is converted by nitrous acid into isopropyl alcohol; normal propylamine into a mixture of normal and isopropyl alcohols (p. 1676).

PROPYL-BENZENE, $C^9H^{12} = C^6H^5.CH^2.CH^2.CH^3$. This hydrocarbon, originally obtained by the action of sodium and propyl iodide on bromobenzene (vi. 295), may also be prepared by dropping benzyl chloride (about 60 g.) into zinc-ethyl previously raised to a gentle heat, decomposing the product with water, distilling in a stream of aqueous vapour, drying, and fractionating over sodium. It then boils at 156.5°–158.5° (corr.), and has a density of 0.881 at 0°. Heated with sulphuric acid (50 grams to a mixture of 40 ordinary and 50 fuming acid), it yields two isomeric propylbenzene-sulphonic acids, one of which (α) forms an anhydrous barium salt crystallising in lamellæ, while the barium salt of the β -acid crystallises with 2 mols. water in microscopic prisms, and is more soluble than the α -salt. The α -lead salt crystallises with 1 mol. water in scales, and is much more soluble than the β -salt, which contains 2 mols. water. The α -potassium salt fused with potash yields a propyl-phenol, $C^6H^4(C^3H^7)OH$, isomeric with cumophenol (p. 593), boiling at about 230°, and yielding a methyl-derivative which boils at 210°–215° (Paternò a. Spica, *Gazz. chim. ital.* 1877, 21).

When bromine-vapour is passed into propyl-benzene heated to 150°–160°, bromopropyl-benzene or phenyl-bromopropyl, $C^6H^5.C^3H^6Br$ is formed, which is resolved on boiling into hydrogen bromide and allyl-benzene, $C^6H^5.C^3H^5$, a colourless liquid having a peculiar odour, boiling under a pressure of 728 mm. at 164.5°–165.5°, having a density of 0.924 at 16°, and a vapour-density = 4.01. *Allyl-benzene dibromide*, or *Phenyl-dibromopropyl*, $C^6H^5.C^3H^4Br_2$, obtained by dropping the calculated quantity of bromine into allyl-benzene diluted with chloroform, crystallises from alcohol in long white silky needles melting at 65°–66°. The same compound is obtained by the action of 2 mols. bromine on 1 mol. propyl-benzene at 160°. The action of bromine on propyl-benzene gives rise also to products of still higher boiling point, one of which boils at 220°, and appears to consist of *bromopropyl-benzene*, $C^6H^5.C^3H^6Br$ (Radziszewski, *Ber.* vii. 143).

Secondary Propyl-benzene Alcohol, or *Phenyl-ethyl Carbinol*, $C^6H^{12}O = C^6H^5.CHOH.C^2H^5$, formed by the action of sodium-amalgam on phenyl-ethyl ketone (propiophenone, p. 1152), boils at 212° , and has a density of 0.99 at 15° (Th. D. Barry, *Ber.* vi. 1006).

Propylisopropylbenzene, $C^{12}H^{18} = C^6H^4 \begin{smallmatrix} CH^2.CH^2.CH^3 \\ CH(CH^3)^2 \end{smallmatrix}$, is formed by the action of zinc-ethyl on cymyl chloride:



The reaction is violent, so that the zinc-ethyl must be added by drops to the cooled liquid. Propylisopropylbenzene boils between 211° and 212° (corr. at 745 mm.), and has a density of 0.8713 at 0° . By oxidation with nitric acid (4 vols. acid with 6-7 vols. water) it is converted into propylbenzoic acid, $C^6H^7.C^6H^4.COOH$ (*infra*), and homoterephthalic acid, $C^6H^4 \begin{smallmatrix} CH^2.COOH \\ COOH \end{smallmatrix}$ (p. 1616) (Paternò a. Spica, *Gazz. chim. ital.* 1876, 99; 1877, 361).

Isopropyl-allyl-benzene, $C^6H^4(C^2H^5)CH=CH-CH^3$, and *Isopropyl-butenyl-benzene*, $C^6H^4(C^2H^5)CH=CH.CH^2.CH^3$, are formed by the action of sodium carbonate on hydrobromocumenylcrotonic and hydrobromocumenylangelic acid respectively (p. 499).

PROPYLBENZOIC ACID, $C^6H^7.C^6H^4.COOH$, isomeric with cumic acid, is formed, as above stated, by oxidation of propylisopropyl-benzene. It crystallises in smooth colourless needles, easily soluble in ether, alcohol, benzene, and chloroform, sparingly in water; melts at 135° - 139° . Its *ammonium salt* is soluble in water, alcohol, and ether, and its concentrated solution gives precipitates with the salts of the heavy metals. The composition of the *silver salt* is $C^6H^7.C^6H^4.COOAg$; that of the *barium salt*, $(C^6H^7.C^6H^4.COO)^2Ba + 2H^2O$ (Paternò a. Spica).

PROPYLENE, $C^3H^6 = CH^2-CH=CH^2$. According to Kerstein (*Ber.* ix. 695), this hydrocarbon is obtained, mixed with hydrogen, by heating glycerol with zinc-dust. The dibromide obtained from it boiled at 142° .

On *Propylene Dichlorides* and *Dibromides*, see PROPANES, CHLORO- and BROMO- (pp. 1671-1673).

Bromopropylenes, C^3H^5Br . The α -compound, $CH^3.CBr=CH^2$, is best prepared by heating α -dibromopropane for five or six hours at 100° with sodium ethylate containing exactly the quantity of sodium necessary to remove one-half of the bromine. The product, when distilled and washed with water, gives, after several rectifications, the α -bromopropylene in a state of purity. It is a mobile liquid, boiling at 47° - 48° under a pressure of 742 mm. Its density is 1.39 at 9° , or 1.362 at 20° . With HBr it gives only one compound, namely, the dibromopropane from which it was originally prepared, boiling at 114.5° ; with bromine it yields the tribromide, $CH^3.CBr^2.CH^2Br$, boiling at 190° - 191° ; sp. gr. 2.33 at 12° .

β -Bromopropylene, $CH^3.CH=CHBr$.—Ordinary bromopropylene, derived from the ordinary dibromide (γ) by loss of HBr , is a mixture of the two bromo-derivatives, $CH^3.CBr=CH^2$ and $CH^3.CH=CHBr$, which, on account of the proximity of their boiling points, cannot be separated by fractional distillation. The separation may, however, be effected by taking advantage of the double fact that HBr attaches itself much more rapidly to α -bromopropylene than to its isomeride (β), and that the combination formed with the first compound is the more stable of the two. By thus sacrificing a portion of the β -bromopropylene, the whole of the first compound (α) may be completely removed.

The mixture of the three bromides resulting from the addition of HBr to ordinary bromopropylene may be distilled, and the portion boiling under 135° collected and decomposed by rapid distillation with concentrated alcoholic potash. Under these conditions the two isomerides of α -dibromopropane are completely destroyed, while the latter is only partially acted on. By fractionating the distillate, the α -dibromocompound boiling at 114° may be readily separated. This, when broken up by potash or by sodium ethylate, yields pure α -bromopropylene boiling at 47° - 48° .

By treating β -bromopropylene with bromine in the cold, the tribromopropane, $CH^3.CHBr.CHBr^2$, is obtained. It boils at 200° - 201° , or 10° higher than the isomeride furnished by α -bromopropylene. Its density is 2.356 at 18° (Reboul).

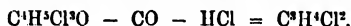
Chloropropylenes, C^3H^5Cl . Three of these compounds, α , β , γ , are known, produced by the action of alcoholic potash (abstraction of HCl) on the corresponding propylene dichlorides or dichloropropanes (Reboul, p. 1671).

α-Chloropropylene, $\text{CH}^3.\text{CCl}=\text{CH}^2$, thus prepared from $\text{CH}^3.\text{CCl}^2.\text{CH}^3$, boils at 25° ; unites with HBr , forming the chlorobromide, $\text{CH}^3.\text{CClBr}.\text{CH}^2$ (b. p. 93°), and with Br^2 forming the dibromide, $\text{CH}^3.\text{CClBr}.\text{CH}^2\text{Br}$ (b. p. 169° – 170°).

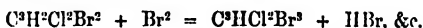
β-Chloropropylene, $\text{CH}^3.\text{CH}=\text{CHCl}$, prepared by heating *β*-dichloropropane, $\text{CH}^3.\text{CH}^2.\text{CHCl}^2$, for four or five hours under pressure with excess of alcoholic potash, is a very mobile liquid lighter than water, and boiling at 35° – 36° . It unites with HBr , forming the chlorobromide, $\text{CH}^3.\text{CH}^2.\text{CHClBr}$, which boils at 110° , together with a small quantity of $\text{CH}^3.\text{CHBr}.\text{CH}^2\text{Cl}$, which passes over at about 121° . *β*-Chloropropylene unites with bromine at 15° , forming the dibromide, $\text{CH}^3.\text{CHBr}.\text{CHClBr}$, which boils at 177° – 177.5° . *γ*-Dichloropropane, $\text{CH}^3.\text{CHCl}.\text{CH}^2\text{Cl}$ (ordinary propylene chloride), in which the two chlorine-atoms belong to adjacent carbon-groups, yields a mixture of *α*- and *β*-chloropropylene, the former predominating.

γ-Chloropropylene, $\text{CH}^3=\text{CH}.\text{CH}^2\text{Cl}$, is identical with allyl chloride.

Dichloropropylene, $\text{C}^3\text{H}^4\text{Cl}^2$ (Pinner, *Liebig's Annalen*, clxxix. 47).—This compound is formed, with separation of hydrochloric acid and carbon monoxide (production of formic acid), by the action of potash- or soda-ley on butylic chloral:



It is readily acted on by 1 mol. bromine at ordinary temperatures, yielding dichlorodibromopropylene, $\text{C}^3\text{H}^2\text{Cl}^2\text{Br}^2$, a colourless heavy oil, which boils at 188° ; when heated in a sealed tube with excess of bromine, it yields more highly brominated substitution-products:



Dichlorodibromopropylene is easily decomposed by alcoholic potash, forming a precipitate of potassium bromide; and if after the reaction is complete the alcohol be diluted with 4 to 6 vols. water, monobromodichlorallylene, $\text{C}^3\text{HCl}^2\text{Br}$, separates as a heavy oil having an agreeable odour like that of chloroform, boiling without decomposition at 143° , and capable of uniting with 2 at. bromine to form dichlorotribromopropylene, $\text{C}^3\text{HCl}^2\text{Br}^3$. This latter is a finely-crystallised body, melting at 207° , moderately soluble in cold alcohol, volatilising with alcohol, and emitting vapours which excite a copious flow of tears.

Dichlorotribromopropylene, treated with alcoholic potash, likewise forms an immediate and copious precipitate of potassium bromide, not however yielding dichlorodibromallylene, $\text{C}^3\text{Cl}^2\text{Br}^2$, by elimination of HBr , but being reconverted into monobromodichlorallylene, $\text{C}^3\text{HCl}^2\text{Br}$, by elimination of Br^2 . Neither can the last atom of hydrogen be removed from $\text{C}^3\text{HCl}^2\text{Br}^2$ by the direct action of bromine, that compound remaining unaltered when heated with bromine for a considerable time in a sealed tube.

Dichloropropylene, agitated with colourless *hypochlorous acid*, is gradually converted into a heavy not very volatile oil, which however consists of tetrachloropropylene, $\text{C}^3\text{H}^2\text{Cl}^4$, evidently resulting from the action of chlorine set free by decomposition of the hypochlorous acid.

Action of Nitric Acid.—When dichloropropylene is slowly dropped into well-cooled nitric acid, a vigorous action takes place, a clear solution being formed, from which a greenish oil is deposited on dilution with water: a portion of the dichloropropylene is however wholly destroyed, much hydrochloric acid being found in the liquid. The oily mass distils between 120° and 200° , with partial decomposition; after treatment with tin and strong hydrochloric acid, however, it does not decompose on heating; by fractional distillation the greater part is found to pass over between 130° and 140° , and at 190° to 195° . The more volatile portion is *trichloropropylene*, $\text{C}^3\text{H}^3\text{Cl}^3$, boiling at 120° , after treatment with caustic potash. The higher-boiling substance solidifies on cooling to a camphor-like mass, possessing an odour like that of chloropicrin; it is very soluble in alcohol, and on analysis gives numbers agreeing with the formula $\text{C}^3\text{H}^4\text{Cl}^3\text{NO}^2$, or $\text{C}^3\text{H}^2\text{Cl}^3\text{NO}^2$, better with the latter, whence apparently the body is trichloronitropropylene; on treatment with caustic soda, it furnishes common salt and a body having the composition of dichloronitroallylene (b. p. 162°), formed from trichloronitropropylene by loss of the element of hydrochloric acid.

The reducing action of the tin converts a portion of the trichloronitropropylene into trichloramidopropylene, $\text{C}^3\text{H}^2\text{Cl}^3(\text{NH}^2)$; this is an oily base, slightly soluble in water, and forming a hydrochloride excessively soluble in water, readily soluble in alcohol; at 100° this salt decomposes into its components; it forms a platinochloride, readily soluble in water and alcohol, crystallising in yellow prisms.

PROPYLENE GLYCOLS, $C^3H^4(OH)^2$. 1. *Ordinary Propylene Glycol*, $CH^3.CH(OH).CH^2.OH$, boils, according to Flawitzky, at 185.3° (at 188° – 189° , Wurz, v. 892). By potassium dichromate it is ultimately oxidised to acetic acid. With dehydrating agents it yields propionic aldehyde (Flawitzky, *Ber.* xi. 1256). 2. *Normal Propylene Glycol*, or *Trimethylene Glycol*, $CH^2.OH.CH^2.CH^2.OH$. Reboul (*Compt. rend.* lxxix. 169) prepares this compound by heating normal propylene bromide with potassium acetate, either in a reflux apparatus or in a sealed tube at the temperature of boiling water, and saponifying the resulting diacetate, $CH^2(CH^2.O.C^2H^3O)^2$, with barium hydroxide. This glycol boils at 216° (corr.), and forms a very thick colourless liquid having a sweet taste, a density of 1.053 at 19° , and miscible in all proportions with water and alcohol.

Normal Propylenic Ethers. The *diacetate* may be prepared as above, or better by the action of trimethylene bromide on silver acetate at 100° in presence of acetic acid. It is a colourless oily liquid, of sp. gr. 1.070 at 19° , boiling at 209° – 210° (corr.), soluble in 8 to 10 vols. of water. The *dibenzoate*, $CH^2(CH^2.O.C^2H^3O)^2$, is prepared, like the diacetate, with silver benzoate, with addition of anhydrous ether, and crystallises from the product—after separation of silver bromide and ether—in a vacuum over sulphuric acid. By recrystallisation from ether it is obtained in fine laminar crystals melting at 53° . The *divalérate* and *monovalérate* are formed together, in like manner, from silver valérate. They are oily liquids, of unpleasant odour, insoluble in water, the former boiling at 260° , the latter at 280° .

Propylene Chlorhydrin, $CH^2OH.CH^2.CH^2Cl$, is formed, together with the corresponding dichloride, $CH^2Cl.CH^2.CH^2Cl$ (p. 1671), by saturating the corresponding glycol with dry hydrogen chloride, heating the solution at 100° in a closed vessel for several hours, again saturating it with hydrochloric acid, and heating a second time. Two layers are then formed, the lower after rectification yielding the dichloride, while the upper, on fractional distillation, yields the chlorhydrin, C^3H^7ClO , which boils at 160° (corr.), has a density of 1.132 at 17° , and dissolves in 2 pts. of water.

Normal Propylene Oxide, $CH^2\langle\begin{smallmatrix} CH^2 \\ CH^2 \end{smallmatrix}\rangle O$, is formed on heating the chlorhydrin with potassium hydroxide, but is instantly polymerised if a little water is present. It is best therefore to use solid potassium hydroxide, and distil after the reaction into a well-cooled receiver. The distillate, when dried over potassium carbonate and rectified, forms a very mobile colourless liquid having a penetrating odour, soluble in water in all proportions, and boiling at 50° .

PROPYL-EUGENOL, $C^9H^{14}(OC^2H^7)(OCH^3)C^3H^5$. See EUGENOL (p. 763).

PROPYL-NITROLIC ACID, $CH^3.CH^2.C\langle\begin{smallmatrix} N.OH \\ NO^2 \end{smallmatrix}\rangle$, and **PROPYL-PSEUDONITROL**, $CH^3.C(CH^3)(NO^2)(NO)$. See PARAFFINS (NITRO-), p. 1494.

PROPYL-PHENOL, $C^9H^{14}\langle\begin{smallmatrix} C^3H^7 \\ OH \end{smallmatrix}\rangle$. This compound, metameric with propyl phenate, $C^6H^5.OC^3H^7$, and isomeric with cumophenol (p. 1542), is formed by fusing the potassium salt of α -propylbenzenesulphonic acid (p. 1678) with potassium hydroxide. It boils at about 230° , and forms a methyl-derivativo boiling at 210° – 215° (Paternò a. Spica, *Gazz. chim. ital.* 1877, 21).

PROPYL-PHENYL KETONE, or *Butyrophenone*, $C^9H^7.CO.C^6H^5$. See KETONES (p. 1152).

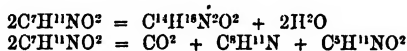
PROTEIDS or **ALBUMINOIDS**. Nasse's experiments (*Pflüger's Archiv. f. Physiologie*, vi. 589) on the decomposition of these bodies by baryta-water, and the conclusions thence deducible as to the state of the nitrogen contained in them, have been already noticed in this Dictionary (vii. 1022). More extended researches on this mode of decomposition, and the light which it throws on the proximate constitution of the proteids, have been made by Schützenberger (*Ann. Chim. Phys.* [5], xvi. 289–419; *Chem. Soc. J.* xxxvi. 542–548).

Coagulated albumin, or other proteid, was heated with the alkaline solution for some hours in an autoclave, whereby ammonia and acetic acid were obtained, together with a light-yellow friable residue, containing all the fixed principles, such as leucine, tyrosine, &c., formed at the expense of the organic matter. The total weight of this residue amounted to about 96 per cent. of the albumin used, whence it appears that the decomposition of albumin under the influence of baryta is accompanied by fixation of the elements of water, the sum of the separate components always exhibiting an excess varying from 10 to 14 per cent. The main results of the analysis of this fixed residue are as follows:

1. The mixture of fixed principles derived from albumin by hydration contains

only amido-derivatives. 2. These derivatives may be divided into two portions, one, the weight of which amounts to about 16 to 18 per cent., containing the substances in which the ratio of nitrogen to oxygen is 1 : 3 or 1 : 4 or 2 : 5. This, which is the more important fraction, consists of acids of the formulae $C^mH^{2m-1}NO^4$, $C^mH^{2m-2}NO^3$, $C^mH^{2m-3}NO^2$, and $C^mH^{2m-4}NO$, the third term being only a molecular combination of the second and fourth. The second fraction, constituting four-fifths of the fixed residue, may be represented by the general formula $xC^mH^{2m}N^2O^4$, the value of x being a little less than 9. As the limit of hydration is approached, the products belonging to the type $C^mH^{2m}N^2O^4$ (where m is a multiple of n) are progressively resolved into simpler bodies, apparently belonging to the same type, and these again into bodies of the type $C^mH^{2m}N^2O^4$, which in their turn are resolved into leucines [or alanines], $C^mH^{2m+1}NO^2$, and leuceines, $C^mH^{2m-1}NO^2$. This interpretation is not affected by the presence of more highly oxygenated acids in the fixed residue, since they may be regarded as derived from any of these bodies by substitution of O for H².

The bodies most easily separated from the fixed residue were tyrosine and leucine, $C^6H^7NO^2$, the former to the amount of 2.3 to 3.5 per cent.; and the successive crystalline deposits, obtained by progressively concentrating the solutions from which the leucine, &c., had been partially separated, were composed of amido-valeric and amido-butyric acids, together with two definite, crystallisable products belonging respectively to the types $C^mH^{2m-2}NO^2$ and $C^mH^{2m-1}NO^2$, viz. tyro-leucine, $C^7H^{11}NO^2$, and a body represented by the formula $C^6H^{11}NO^2$; the quantity of tyro-leucine obtained was about 60 or 70 grams from 10 kilograms of albumin. Tyro-leucine is a white crystalline deposit of chalky aspect, nearly tasteless, soluble in about 20 pts. of water at 15°. It melts and decomposes at 210°, breaking up into a white sublimate and a volatile oily base having an odour of radish and leaving an abundant yellow vitreous residue. The analysis of the chloroplatinate of this base gives it the formula of collidine, $C^6H^{11}N$, and that of the vitreous residue gives the formula $C^6H^{11}N^2O^2$. The decomposition of tyro-leucine may therefore be regarded as proceeding thus—



whence it may be supposed that tyro-leucine is a compound of amido-valeric acid with a body of the formula $C^6H^{11}NO^2$, differing from tyrosine only by an atom of oxygen. This is rendered more probable by the fact that tyrosine, when heated under similar conditions, breaks up into CO^2 and a base, $C^6H^{11}NO$, which differs from collidine only by an atom of oxygen.

Among the homologues of leucine, amido-valeric and amido-butyric acids were met with in quantity, but amido-propionic acid in very small proportion only.

The leuceines may be regarded as amido-acids of the acrylic, or of an isomeric series. They reduce ammoniacal silver nitrate on warming, and are attacked by bromine in the cold, yielding HBr, and an acid having the formula $C^mH^{2m-1}NO^3$.

Both leucines and leuceines seem to be frequently produced by the splitting up on crystallisation of bodies of the formula $C^mH^{2m}N^2O^4$ ($m=10$ or 12). These bodies have a sweet taste, and are thence called by Schützenberger glucoproteins; they crystallise less easily than the leucines, especially the lower terms; they are very soluble in water, but almost insoluble in cold absolute alcohol; alcohol of 90 per cent. however dissolves them with ease.

Another substance resulting from the decomposition of albumin, which is produced in considerable quantity, is a yellow viscous body obtained by precipitating certain mother-liquors from which leucines have been crystallised by ether. Dried at 120°, it is converted into a transparent amorphous mass, which on analysis gives numbers comprised between the formulae $C^6H^6NO^2$ and $C^6H^7NO^2$, very often sensibly approximating to $C^6H^{10}N^2O^4$; it appears in fact to be constituted in great part of butyric leucine with an admixture of some superior homologue.

The longer the action of baryta on albumin is continued, and the more concentrated the solution, the greater is the proportion of leucines and leuceines formed, whilst under the contrary conditions, the intermediate bodies, or glucoproteins, constitute the bulk of the fixed residue, representing the initial terms of the hydration of albumin; under all circumstances caproic leucine and tyrosine appear to be the ultimate terms of the decomposition.

The mechanism of the reaction would therefore appear to admit of the following explanation. The albuminoid molecule losing ammonia and carbon as carbonic, oxalic, and acetic acids, and assimilating water, is converted into a comparatively simple mixture of glucoproteins, $C^mH^{2m}N^2O^4$, containing as its principal term $C^6H^{10}N^2O^4$: by the prolonged action of baryta and a high temperature, these glucoproteins split up partly into leucines and leuceines, and partly into double compounds formed by the union of glucoproteins and leuceines with the leucines.

Schützenberger regards albumin as an imido-derivative, which by hydration is changed into a mixture of amido-derivatives.

On the reaction of Proteïds with Bromine, see W. Knop (*Chem. Centr.* 1875, 395, 411, 426; *Jahresb. f. Chem.* 1875, 810).

Digestion of Proteïds.—All proteïds hitherto examined may be resolved by the action of acid gastric juice (pepsin and hydrochloric acid) into two bodies or groups of bodies. On the one hand, there are formed the known decomposition-products of proteïds, viz., the soluble peptones, acid-albumins, &c., while, on the other, a sharply defined portion remains undigestible. This latter appears to contain, together with nitrogen and phosphorus, a compound nearly related to nucleïn (A. Stutzer, *Ber.* xiii. 251).

Action of Alkaloids on Proteïds.—According to M. J. Rossbach (*N. Rep. Pharm.* xxii. 512), the proteïds contained in the various tissues of the body and in the protoplasm, lose their affinity for ozone under the influence of alkaloids at 30°–40°, and at higher temperatures, but below that at which ordinary albumin coagulates they are precipitated in combination with the alkaloids. These reactions are subject to numerous variations according to the particular proteïds and alkaloids concerned in them. The combination of ozone with *hæmoglobin* is strengthened by alkaloids, and its transference therefrom to other bodies more or less prevented. The diminution of oxidability of the protoplasm by alkaloids is therefore determined by the alteration of the proteïds, and the increased stability of the combination of ozone with *hæmoglobin*.

Compounds with Cupric Oxide.—Compounds of legumin, conglutin, and gluten-casein with cupric oxide have been prepared by H. Ritthausen (*J. pr. Chem.* [2], v. 215). These bodies are precipitated by solution of cupric sulphate from nearly all liquids containing proteïds, provided that the acids or alkalis used to hold the proteïds in solution are present only in slight excess. The three modifications of plant-casein just mentioned react very differently with cupric solutions. Legumin in combination with cupric oxide not only remains unaltered, but shows little inclination to dissolve in water; conglutin suffers partial decomposition, attended with elimination of ammonia, and becomes somewhat soluble in water; gluten-casein is but very slightly altered, but dissolves in water in considerable quantity. These observations have been extended by Ritthausen and Pott (*J. pr. Chem.* [2], vii. 361) to the compounds of cupric oxide with milk-casein and with the proteïds which are soluble in alcohol and water. These compounds dissolve in cold dilute potash-ley and are precipitated unaltered on neutralisation. The quantity of cupric oxide which a proteïd can take up, with formation of a soluble compound, is distinctly limited, and of various amount for different proteïds. The compounds in question are well adapted for the quantitative estimation of proteïds. According to Stutzer (*Ber.* xiii. 251), the method of precipitation with cupric salts may be advantageously applied to the separation of proteïds from other nitrogen-compounds occurring in plants, e.g. amygdalin, solanin, leucine, tyrosine, asparagine, alkaloids, thiocarbamides, nitrates, ammonia-salts.

Optical and Chemical Characters of certain Proteïds, especially of Dialysed Albumins.—The following observations have been made by H. Haas (*Chem. Centr.* 1876, 295, 811, 824). (1). Egg-albumin and serum-albumin cannot be freed by dialysis from the whole of their inorganic salts, the dry albumin obtained from the dialysed solutions yielding on the average 1 per cent. of ash. (2). Albumin-solutions freed from salts as completely as possible, exhibit, on boiling, or on addition of alcohol, at least a strong opalescence, and in most cases strong turbidity and even precipitation. The alteration thus exhibited by albumin in presence of only small quantities of salts is the same as that exhibited by natural solutions of albumin, although the two liquids may differ in external appearance; the change which takes place in a solution of albumin, freed as far as possible from salts, must, therefore, also be regarded as coagulation. (3). The flocculent precipitation of albumin by hydrochloric acid or an acid phosphate is mainly dependent on the quantitative relation between the albumin and the precipitant, and is altogether independent of the concentration of the solution. The precipitation of albumin by acids in the form of flocks may therefore be regarded as a chemical process, whereas its precipitation by salts depends upon the proportion of water present, and must be looked upon as a physical change. (4). The albumin at the end of the dialysis often exhibits an acid reaction, even when an excess of alkali or alkaline carbonate was before present, but it is not yet determined whether the acid reaction belongs to the albumin itself or is determined by the presence of foreign substances. From his own experiments, Haas inclines to the view that the reaction of pure albumin-solutions is neutral. (5). The specific rotatory power of egg-albumin is -38.08° ; that of serum-albumin was found in two experiments to be -62° , in a third -55.75° ; that of *fibrinogen-substance*, prepared from an ascitic fluid,

was -59.75° ; that of sodium albuminate -55° . (6). The specific rotatory power of natural albumin-solutions is not altered by the salts which they contain, no matter in what quantity these salts may be present.

Comparison between Animal and Vegetable Proteïds.—The following analyses of albumin, casein, and fibrin of animal and vegetable origin, agreeing nearly with those of other chemists (i. 67, 811; ii. 640; vi. 975), have been made by A. Brittner (*N. Rep. Pharm.* xxi. 66–108 and 129–150):

	C	H	N	O	S
Egg-albumin	54.00	16.55	6.99	22.82	1.63
Blood-albumin	53.60	15.60	7.14	22.46	1.30
Plant-albumin	54.98	15.84	7.31	20.65	1.22
Blood-fibrin	52.40	18.07	7.03	21.29	1.22
Plant-fibrin	53.82	16.04	7.30	21.80	1.04
Animal-casein	54.67	15.78	7.46	22.97	1.12
Plant-casein	53.94	16.47	7.16	21.93	0.50

From these numbers it is inferred that the proteïds of the animal organism are merely modifications of those previously formed in the plant.

With regard to the properties characteristic of the members of these several groups, Brittner makes the following remarks: Blood-fibrin and plant-fibrin react in exactly the same manner as egg-, blood-, and plant-albumin, with strong hydrochloric and strong nitric acid at the boiling heat; with aqueous solution of iodine; with a mixture of sugar and dilute sulphuric acid on heating; with alkaline solution of cupric sulphate; and with Millon's reagent (vi. 970, footnote). Solutions of casein and legumin are precipitated, like solutions of albumin, by alcohol, tannic acids, mineral acids, and metallic salts,—also by organic acids, which is not the case with albumin. Casein dissolves both in alkaline liquids and in very dilute acids, but not in water.

Comparative observations on proteïds of animal and vegetable origin have also been made by Th. Weyl (*Pflüger's Archiv. f. Physiologie*, xii. 635; *Zeitschr. physiol. Chemie*, i. 72).

Vitellin, from egg-yolk dissolved in dilute aqueous sodium chloride, coagulates at 75° if the solution is neutral; on gradually raising the temperature, partial coagulation-takes place at 70° , but if the heat be quickly increased, coagulation does not commence below 80° . A body resembling vitellin in all known reactions was found in human amniotic liquor in a case of disease. Vitellin dissolved in solution of common salt and precipitated by water is easily converted, on prolonged immersion in water, into an albuminate (casein); it is then insoluble in solution of sodium chloride, but dissolves in a 1 per cent. solution of sodium carbonate. Recently prepared vitellin, dissolved in a 1 per cent. solution of sodium carbonate, is but slowly precipitated by water alone, but on passing carbon dioxide into the solution, an abundant precipitation takes place. On adding a drop of sodium carbonate solution to water in which vitellin is suspended, the liquid immediately becomes clear, but soon again turbid, and clarifies itself on repeated addition of the alkaline carbonate, becoming turbid again soon after. This effect may be repeated three or four times in the same liquid, and appears to be peculiar to globulins dissolved in a 1 per cent. solution of sodium carbonate and reprecipitated by carbonic acid. Myosin from horse-flesh, dissolved in a 10 per cent. solution of sodium carbonate, coagulates at 55° – 60° , and is converted by prolonged contact with water into albuminate, and then becomes insoluble in dilute solution of common salt: it is not so easily precipitated by water as vitellin. Weyl has never been able to detect it in albuminous urine. Serum-globulin, prepared from the serum of ox-blood by diluting with water, neutralising with acetic acid, and passing carbon dioxide into the liquid, dissolves in a 10 per cent. solution of sodium chloride, and is precipitated therefrom by water or by saturation with sodium chloride, incompletely, however, in the latter case. The neutral solution coagulates at 75° . Serum-globulin is converted by prolonged contact with water into albuminate; after drying in a vacuum over sulphuric acid, it may be heated gradually up to 100° without alteration of its properties. Serum-casein, prepared according to Kühne's directions, agrees in all its reactions with Kühne's globulin. Since now paraglobulin (fibrinoplastic substance) differs from Kühne's globulin only by the admixture of the fibrin-ferment, and as, moreover, no difference has hitherto been made out between globulin and serum-casein, it follows that blood-serum contains only one globulin-substance, namely, serum-globulin.

The existence of vegetable proteïds soluble in water, like egg-albumin, has not hitherto been demonstrated. Plant-globulins exhibit the same reactions as animal globulins and animal proteïds in general. Plant-vitellin, extracted by common salt solution from the seeds of oats, maize, peas, white mustard, and Para nuts, agrees in

all its reactions with vitellin from egg-yolk. The proteids of the Para nut contain membraneless crystals consisting of vitellin, reacting like animal vitellin, and melting at 75° . The membrane of the crystals, which forms only after prolonged contact with water, is a precipitated membrane. The vitellin-crystals are doubly refractive. The ash of vitellin consists mainly of phosphates mechanically mixed with the organic substance. Elementary analysis gave for the pure vitellin, 52.43 per cent. C., 7.12 H., 18.1 N., 0.55 S. The vitellin analysed was free from nuclein and lecithin, and may therefore be regarded as the purest globulin-substance yet known. The seeds of wheat, peas, oats, white mustard, and sweet almonds contain also a second proteid, viz. plant-myosin, which exhibits all the reactions of the myosin of non-striated muscles (iii. 1066), and coagulates at 55° – 60° . Fresh seeds contain no proteids of the casein-group (albuminate). All the substances hitherto designated as plant-casein are artificial products, or have been formed in the seeds by secondary processes, having nothing to do with the natural development of the plant. In contact with water, acids, or alkalis, all globulins, animal or vegetable, are probably converted first into albuminates, afterwards into coagulated proteids.

Ritthausen (*Chem. Centr.* 1877, 567, 586) criticises these results, and likewise controverts the views of Hoppe-Seyler, who, in his 'Physiologische Chemie' (I. Theil, s. 75) regards the proteids contained in buds, young shoots, and seeds as globulin-substances, and expresses the opinion that Ritthausen's statements respecting the vegetable proteids are founded on the analysis, not of pure unaltered proteids, but of substances more or less decomposed and imperfectly purified. Ritthausen, on the other hand, defends his method of preparing vegetable proteids, and on the ground of numerous elementary analyses, regards vegetable proteids as different from those of animal origin.

Transformation of Proteids in the Bodies of Ruminants.—Experiments on goats by Stohmann, Frühling a. Rost (*Landw. Vers.-St.* xii. 396), have led to the following results: 1. The total quantity of albumin decomposed in the body appears as oxidation-products in the liquid and solid excrements. 2. The transformation of albuminous matter is dependent on the quantity of albumin contained in the circulation. 3. The transformation of nitrogenous matter is accelerated by an increase in the quantity of water imbibed. 4. The excretion of nitrogen quickly adapts itself to an increase or nitrogen in the food. 5. With an insufficiency of albumin in the food, the body becomes poorer in albumin. 6. Considerable increase in weight takes place when, together with a sufficiency of albumin, large quantities of non-nitrogenous matters are given. These experiments show that, with regard to the transformation of albuminous matters in the organism, no difference exists between carnivorous and herbivorous animals, excepting that, in the latter, part of the nitrogen leaves the body in the form of hippuric acid.

Albumin. *Reaction with Potassium Hydroxide.*—Kühne, by fusing albumin with potash, obtained a body which he regarded as an isomeride of indole, and designated as *pseudo-indole*; and a similar result was obtained by Engler a. Junecke (p. 1089). According to Nencki, however (*J. pr. Chem.* [2], xvii. 97), the product thus obtained is not a single substance, but a mixture of indole with a body called *skatole* (q.v.), obtained also from excrements. Nencki also finds that when fused potash acts on albumin, leucine and tyrosine are formed, in addition to peptones, and that, by further action, volatile fatty acids, especially valeric acid, are produced, with evolution of hydrogen, indole and *skatole* being formed at the same time. If the fusion is continued for a long time, the amount of peptone-like bodies decreases, and the leucine and valeric acid are gradually converted into butyric acid. The tyrosine is perfectly decomposed, and phenol appears instead. The latter body is probably formed from the tyrosine, since whenever phenol is produced, whether by putrefaction or by the action of potash, tyrosine is wanting, and *vice versa*.

On the reactions of Albumin with baryta-water, see p. 1681; with chloral, p. 439.

Oxidation.—By oxidation with ammonium permanganate albumin is converted into carbamic acid (p. 382).

Reaction with Cyanogen.—Experiments by O. Loew (*J. pr. Chem.* [2], xvi. 60) on the action of cyanogen on albumin, have led to the following results: (1). Cyanogen is directly taken up by albumin, with simultaneous formation of water. (2). The resulting addition-product, when treated with alkalis, gives up the water and part of the cyanogen, yielding peculiar non-nitrogenised bodies. (3). An atomic group of small molecular weight separates from the albumin, taking up at the same time a relatively large quantity of cyanogen and water (*oxamöidin*).

Coagulation.—Mathieu a. Urbain (*Compt. rend.* lxxvii. 706), by exhausting white of egg with the mercury-pump, obtained considerable quantities of carbon dioxide

together with small quantities of oxygen and nitrogen. They consider that carbon dioxide is the agent which brings about the coagulation of the egg-white on heating, and that coagulated egg-white is a compound of protein-substance with carbon dioxide, mixed with compounds, formed on coagulation, of the protein substance with salts contained in the egg-white. Albumin, exhausted by the mercury-pump of its carbon dioxide and volatile salts (ammonium carbonate and sulphide), reacts like globulin, which indeed appears to be the proteid from which the other bodies of the class are formed by addition of small quantities of various substances.

Gautier, on the other hand (*Bull. Soc. Chim.* [2], xxii. 51), found that dilute solutions of egg-albumin through which a stream of hydrogen was passed for several days still remained coagulable by heat (Urbain, *ibid.* 484, doubts whether this treatment would remove the whole of the carbon dioxide); and he further observes that white of egg dried at a low temperature loses the property of coagulating by heat, but recovers it when carbon dioxide is passed through the solution.

Regeneration of Spoilt Albumin in Print-works. In the process of calico-printing, the cloth soaked in a solution of albumin, and then printed with the dye-stuff, is finally exposed to the action of steam, whereby the albumin is coagulated and the dye-stuff fixed. The success of this process, however, requires that the albumin shall be quite fresh and unspoiled, so that a perfect solution of it may be made before the cloth is steeped in it. Albumin which has become insoluble may indeed be rendered soluble again by the action of alkalis or alkaline carbonates, but at the same time it loses the property of coagulating in the steam-bath, which is indispensable to its use in printing. J. Wagner, however, finds that 350–400 grams of spoilt albumin, placed in contact with 30 grams of cold-washed rennet, suspended in a litre of water to which 10 grams of concentrated hydrochloric acid have been added, passes into solution at a temperature of 37.5° C., and that this liquid, if filtered after standing for twenty-five to thirty hours and neutralised with ammonia, possesses, like the aqueous solution of fresh albumin, the property of coagulating on the steam-bath, and fulfils all technical requirements. According to Witz, pig's stomach acts in this way still more energetically than rennet. It is remarkable that albumin thus dissolved in pepsin is not coagulated by acetic acid. Wagner and Witz also propose to utilise this action of pepsin for freeing spoiled printed goods from the colouring matter fixed on them by coagulated albumin. Blood-fibrin may also be dissolved by means of this reagent more readily than by hydrochloric acid, which, as observed by Bouehardat, is capable by itself of dissolving fibrin (Wagner and Witz, *Dingl. pol. J.* cccix. 166).

Detection and Estimation of Albumin.—To detect albumin in urine, L. Siebold (*Zeitschr. anal. Chem.* 1874, 248) mixes the liquid with potash to slight alkaline reaction, filters, acidulates the filtrate with acetic acid, and heats a portion of it to boiling. If the heated liquid be now compared with a cold portion contained in another tube, the slightest turbidity in the former will be easily detected. A. Hilger (*Arch. Pharm.* [3], vi. 388) has compared the several methods proposed for the detection of albumin in urine, and gives the preference to Boedecker's method, which consists in precipitating the albumin in acetic acid solution with potassium ferrocyanide, observing however that the nitric acid test and the coagulation-test with acetic acid are also worthy of notice.

For quantitative estimation, Girgensohn (*N. Report. Pharm.* xxii. 557) mixes the solution containing the albumin with half its volume of a 20 per cent. solution of common salt; adds tannin in slight excess; collects the precipitate on a weighed filter; washes it with water till free from salt, and then with boiling alcohol, till no more tannin can be detected in the filtrate: the precipitate then consists of pure albumin. In estimating albumin in urine by this method, uric acid must first be removed by adding acetic acid and leaving the liquid in the cold.

All proteids contained in albuminous urine are precipitated by tannin added in slight excess, and the precipitate when treated with boiling alcohol gives up the whole of the tannin. The albumin in the urine of nephritic patients differs from that which occurs in accidental albuminuria, in the proportion in which it combines with tannin, the former taking up 37 and the latter 28 per cent. of that substance. The albumin of eggs, of serum, and of pathological secretions in general combines with 28 per cent. of tannin.

On Bornhardt's method of estimating albumin in solution by the difference of density of the liquid before and after the precipitation of the albumin, see *Zeitschr. anal. Chem.* 1870, 149; 1877, 124; *Jahresb. f. Chem.* 1870, 1056; 1877, 1088.

Trinitro-albumin, $C^{22}H^{103}(NO_2)^3N^{14}SO_2$, is prepared by thoroughly tritulating finely-pulverised and well-dried albumin in a cooled capacious mortar with 14–16 times its weight of hydrogen nitrate, NO_2H , perfectly freed from nitrous acid, or by briskly agitating it therewith in a cooled bottle, and after ten to fifteen minutes

quickly mixing the resulting gelatinous mass with a large quantity of water, whereupon the insoluble light-yellow tasteless trinitro-compound separates out. If the gelatinous mass be left to itself for several hours at a temperature below 10° , a small quantity of nitrogen tetroxide is given off, and a solution is formed, which, when diluted with water, deposits a dark yellow tasteless hydroxytrinitroalbumin, $C^{72}H^{100}(NO_2)^3N^{16}(OH)^2(SO_2.OH)O^{27}$.

Trinitro-albumin dissolves without alteration in dilute alkalis, forming a reddish-yellow solution, from which it is precipitated in yellow flocks on addition of an acid. Its solution in strong hydrochloric acid may be boiled for a considerable time without sensible decomposition. Its solution in strong sulphuric acid, heated for some time and then mixed with water, yields a precipitate richer in sulphur than the original compound. Hydroxytrinitroalbumin exhibits similar reactions (O. Loew, *J. pr. Chem.* [2], v. 433).

On Hexnitro- and Hexamido-albumin-sulphonic acids, see vol. vii. p. 645.

Compounds of Albumin with Acids and Alkalis.—Acid compounds of albumin are formed by pouring a solution of white of egg into a parchment-paper dialyser, and leaving it for twenty-four hours in contact with a dilute acid—e.g. nitric, hydrochloric, sulphuric, orthophosphoric, metaphosphoric, citric, oxalic, acetic, or tartaric acid, contained in an outer vessel. Most of these compounds are gelatinous. For a quantity of albumin represented by Lieberkühn's formula, $C^{72}H^{112}N^{18}SO^{22}$, the compounds contain 2 mols. nitric, 2 mols. hydrochloric, 1 mol. sulphuric, $\frac{2}{3}$ mol. phosphoric acid. They are all precipitated by nitric, sulphuric, hydrochloric, metaphosphoric, and picric acid; some also by potassium ferrocyanide, ammonium chloride, basic lead acetate, mercuric chloride, barium chloride, silver nitrate, alcohol, phenol, and tannin (G. S. Johnson, *Chem. Soc. J.* xxvii. 734).

J. Soyka (*Pflüger's Archiv.* xii. 347) finds, from comparative experiments on acid-albumin and alkali-albuminate (vi. 972), that these bodies exactly resemble one another in their reactions, and that the hitherto assumed difference in their precipitability by acids in presence of an alkaline phosphate has no existence. An alkaline solution either of albuminate or of acid-albumin containing phosphate may be mixed with an acid till acid reaction becomes apparent, without formation of a precipitate. At the limit of precipitability, the still transparent solutions exhibit an amphoteric reaction and contain 9 mols. acid phosphate, (MII^2PO^4) , to 1 mol. normal phosphate, (M^2HPO^4) ; if the relative quantity of the acid phosphate is further increased, precipitation takes place. Soyka proposes to retain the names albuminato and acid-albumin, and to designate as *protein* the body which, in combination with acids, forms acid-albumin, and in combination with a base, albuminate. He considers that, in spite of the concordant reactions of the two, there is no ground for the assumption that acid-albumin and albuminate are identical in composition and constitution. Even if albuminate and acid-albumin prepared from albumin exhibit no differences in their precipitates, such differences become apparent when these precipitates are compared with those of syntonin and albuminate which have been prepared from flesh. Whether these differences arise from a diversity in the proteins of these substances, or are due to admixtures, is a point which cannot yet be decided, as neither the elementary analyses nor the decomposition observed by Nasse (vii. 1023) afford any satisfactory evidence relating to it. Soyka refers the acid-albumins and albuminates to one and the same albuminoid-group (both as above-mentioned containing protein united in the one case with an acid, in the other with a base), and divides the soluble proteins into three groups: *albumins*, *proteins*, and *globulins*.

According to Heynsius (*Arch. néerl.* x. 1), the alkali-albuminates differ from one another according to the concentration of the alkali used in their preparation; paraglobulin is identical with the albuminate obtained with weak alkali. The acid-albumins also differ from one another according to the concentration of the acid used in preparing them.

All albuminates when dissolved in excess of glacial acetic acid, and treated with strong sulphuric acid, exhibit a splendid violet colour and faint fluorescence, and if sufficiently concentrated, an absorption in the spectrum, which, like that of urobilin and the red oxidation-product of bile-pigment (choletelin) lies between the lines B and F. Bodies not chemically related to the albuminates do not exhibit this reaction. Peptones (p. 1688) exhibit it, and must therefore be classed with the albuminates (Adam Kiewicz, *Ber.* viii. 161).

Paralbumin.—This variety of albumin, which Scherer obtained from an ovarian cyst (i. 68), exhibits, according to Huppert (*Zeitschr. anal. Chem.* xvi. 248) the following characteristic reactions: (1). It does not separate on boiling from a solution to which acetic acid has been added, differing therein from serum-albumin, which by proper regulation of the quantity of acetic acid, may be completely separated on boiling in

large flakes, the liquid becoming quite clear; a solution of paralbumin similarly treated always remains milky whatever may be the quantity of acetic acid added. (2). When a liquid containing paralbumin is digested for some time in a water-bath with hydrochloric acid of 0.1 per cent., sugar is produced. Paralbumin is not peculiar to ovarian cysts, but occurs also in other cysts, and in the liquid of ascites.

Casein. The identity of casein with potassium albuminate, on which doubts have been thrown (vi. 973), is confirmed by the following facts: (1). Both casein from milk and artificially prepared potassium albuminate are precipitated from alkaline solutions by rennet. (2). Neither of them is precipitated by sodium carbonate. (3). The filtration of the two bodies through cells of porous earthenware is influenced by the same circumstances. (4). Both are decomposed by alkaline hydroxides under otherwise similar circumstances, with formation of a sulphide of alkali-metal. (5). The differences observed in the optical rotatory power of the two are not sufficient to show that they are distinct bodies (Soxhlet, *J. pr. Chem.* [2], vi. 1).

According to Béchamp (*Compt. rend.* lxxviii. 1575), casein is decomposed at 140°, part becoming soluble in alkalis, the other not; a small portion of the latter, however, dissolves in acetic acid. A solution of casein in acetic acid yields, on evaporation in a vacuum, an inodorous horny mass having a sour taste. 100 pts. of casein take up 33.1 acetic acid. Butyric acid likewise unites easily with casein.

Conversion of Casein into Albumin.—The addition of a drop of mustard-oil to 20 grams of cow's milk prevents the coagulation of the milk, and after five to seven weeks, the casein is found to be converted into albumin, the liquid having a strong acid reaction. This transformation of casein appears to be a process of oxidation. If the milk treated with mustard-oil be poured into an earthenware cell standing in a solution of permanganate, considerable quantities of albumin are formed in a few days (Schwalbe, *Ber.* v. 286).

On the Separation of Casein from Milk by Dialysis, see MILK (p. 1326). On the Morphology of Milk-casein, see F. A. Kehler (*Arch. f. Gynäkologie*, ii. 1; *Jahresh. f. Chem.* 1874, 931).

Fibrin. According to J. Goodman (*Rep. Br. Assoc.* 1871, 72), egg-albumin in contact with water is converted in a short time into fibrin; compare Smee (ii. 639). On the other hand, albumin may be produced by decomposition of fibrin. When blood-fibrin is dissolved in salt water, the liquid, mixed with a trace of prussic acid, to prevent putrefaction, and subjected to dialysis till the salt is almost completely removed, the solution thus freed from salt is found to contain two proteids, evidently resulting from the decomposition of the fibrin, one coagulable by heat, precipitated by mineral acids and mercuric chloride, and exhibiting the percentage composition of albumin, while the other is not coagulated by heat and yields an ash rich in calcium phosphate and magnesia (Gautier, *Compt. rend.* lxxix. 227).

Iron in Fibrin.—The proportion of iron in the fibrin, blood-corpuscles, and albumin obtained from the blood of a half-fatted cow has been determined by Boussingault (*Arch. Pharm.* [3], iii. 526). The amounts per cent. in the air-dried substances were found to be:

	Ash	Iron
Fibrin	2.151	0.0466
Corpuscles	1.325	0.3500
Albumin	8.715	0.0863

Pancreatic Digestion.—The products of the pancreatic digestion of fibrin yield a distillate exhibiting the reactions of indole (Nencki, *Ber.* vii. 1593). Other proteids similarly treated likewise yield indole (p. 1089).

On the Coagulation of Fibrin, see A. Schmidt (*Compt. rend.* lxxxiv. 78, 112; *Chem. Soc. J.* xxxi. 483, 726), and O. Hammarsten (*Pflüger's Archiv. f. Physiologie*, xiv. 211-273; *Chem. Soc. J.* xxxi. 726).

On Myosin, see p. 1684.

Peptones. The preparation and reactions of these bodies have been studied by R. Maly (*Liebigs Annalen*, clxxv. 178). To prepare them, purified dry fibrin, after maceration in dilute hydrochloric acid, is digested for two or three days with pepsin, and the resulting solution is neutralised with sodium carbonate, boiled, filtered, and evaporated. It is then subjected to prolonged dialysis to remove chlorides, and the peptone-solution removed from the dialyser is filtered, if necessary, concentrated, and fractionally precipitated with alcohol.

This peptone solution gives with acetic acid and potassium ferrocyanide a precipitate which dissolves in hydrochloric and in nitric acids—a reaction likewise exhibited

by proteïds in their original state. As the mean of several analyses of various peptone-preparations, Maly found 51.40 per cent. C., 6.95 H., and 17.31 N. He regards peptone, not as a mixture of decomposition-products of proteïds, but as a distinct and independent substance, differing but little in elementary composition from the proteïd from which it is produced.

To determine the nutritive value of peptone, respecting which opinions have hitherto been much divided, Maly made experiments on pigeons with peptone prepared from blood-fibrin in the manner above described, the quantity given being exactly equivalent to the albumin in the food previously supplied to the birds. These experiments led to the conclusion that peptone is still an unresolved protein-molecule, capable of replacing albumin, useful and available for the organism, and a product of digestion capable of reconstruction into albumin and assimilation by the organism.

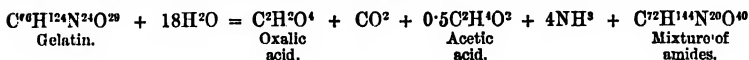
Peptones dissolved in glacial acetic acid, and treated with strong sulphuric acid, exhibit the same violet colour, fluorescence and absorption-spectrum as unaltered proteïds, whereas bodies not related to the proteïds do not exhibit these appearances. Hence it follows that all peptones stand to the proteïds in a closer relation than the products of decomposition of those bodies, such as leucine, tyrosine, &c. (Adamkiewicz, *Ber.* viii. 161).

According to Huppert (*Ber.* vi. 1279), the so-called 'peptone,' obtained by pancreatic digestion of proteïds, is a mixture of leucine, tyrosine, and at least two other substances as far removed from the proteïds as the two just mentioned.

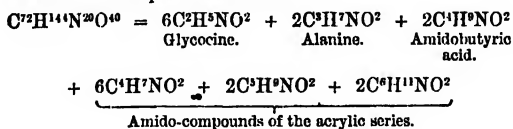
Detection in Urine.—To detect peptones in albuminous urine, Senator (*Zeitschr. anal. Chem.* vii. 474) removes the albumin in the ordinary way, by heating with or without addition of acetic acid, and mixes the filtrate with three times its bulk of alcohol, whereby the peptone is thrown down in the form of a yellow precipitate which is insoluble in alcohol but soluble in water, and is coloured yellow by nitric acid.

Appendix to Proteïds.

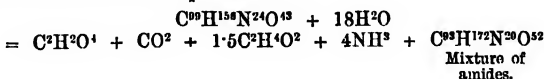
Gelatinous Substances. From experiments by Schützenberger & Bourgeois (*Compt. rend.* lxxii. 262), it appears that when isinglass, ossein, gelatin, and chondrin are decomposed by the method applied by Schützenberger to proteïds (p. 1681), they likewise yield ammonia, carbon dioxide, and oxalic acid, in such proportions as to show that they consist of urea and oxamide. The analysis of the mixture of amido-compounds thus produced shows that the mode of decomposition is nearly the same for isinglass, ossein, and glue, but somewhat different for chondrin. For the first three bodies it may be represented by the equation:



The mixture of amides is composed as follows:



For chondrin the mode of decomposition is:



Gelatin boiled with dilute sulphuric acid yields, according to Gachtgens (*Zeitschr. physiol. Chem.* i. 299), aspartic and glutamic acids in small quantity, a compound $\text{C}^{11}\text{H}^{22}\text{N}^2\text{O}^6$, crystallising in prisms, and two substances agreeing nearly in composition with alanine and amidobutyric acid respectively. Gachtgens thinks it probable that the compound $\text{C}^{11}\text{H}^{22}\text{N}^2\text{O}^6$ may be resolvable by repeated crystallisation into $\text{C}^9\text{H}^7\text{NO}^2$, $\text{C}^4\text{H}^9\text{NO}^2$, and $\text{C}^4\text{H}^7\text{NO}^2$.

According to Bizio (*Gazz. chim. ital.* 1876, 255), a slightly alkaline solution of gelatin reduces mercuric chloride and oxide, with separation of metallic silver.

Nutritive value of Gelatinogenous Tissues, &c.—From experiments by J. Etzinger (*N. Rep. Pharm.* xxiii. 535) it appears that bones, cartilage, and tendons, by virtue of

the gelatinous substance contained in them, play an important part in animal nutrition. Tendons are the most readily digested; bones pass so rapidly through the alimentary canal, that only a small portion of their organic substance is absorbed during the passage. As gelatinous tissues contain but a small proportion of albumin, their nutritive value must be proportional to the quantity of gelatin which can be obtained from them; they are capable of saving a large quantity of albumin, which would be decomposed in their absence.

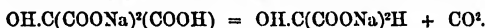
C. Voit (*Zeitschr. f. Biologie*, viii. 297) finds, by feeding experiments on animals, that gelatin is not capable of entirely replacing albumin in nutrition. In the animal body a distinction must be made between circulating albumin and organic albumin. The former is subject to rapid decomposition; the latter is not decomposed as such, but is converted into circulating albumin only when the food does not contain a quantity of albumin sufficient to cover the loss of circulating albumin. If the food contains an excess of albumin, that excess is stored up as organic albumin. Now gelatin can never yield organic albumin, but it may replace the circulating albumin in so far as it prevents the conversion of organic into circulating albumin. In a large dog, 168 pts. of gelatin were found to be capable of replacing 84 pts. of albumin in the food. Gelatin also diminishes the waste of fat in the body, 200 pts. of gelatin acting in the same way as 74 pts. of fat.

PROTocatechuic Acid, or [1 : 3 : 4] DIHYDROXYBENZOIC

ACID, $C^7H^5O^4 = COOH \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2 \end{array} \text{OH}$. On the formation and constitution of this acid, see vii. 431, 932, 1023; viii. 289. On its formation from Narcotine-derivatives, viii. 1384. It is also produced by the action of melting potash on iodoparahydroxybenzaldehyde, $C^7H^5I(OH)(CHO)$ (Tiemann a. Herzfeld, *Ber.* x. 213), on Peruvian guaiac-resin (p. 899), and on angelica-resin (C. Brimmer, *N. Rep. Pharm.* xxiv. 641).

Action of Nitrous gas.—When this gas is passed into an ethereal solution of protocatechuic acid, nitrogen dioxide and carbon dioxide are evolved, and a complicated reaction takes place, resulting in the formation of oxalic acid, carboxytartronic acid, dinitrodihydroxyquinone, trinitrophenol, α -dinitrophenol, and nitrohydroxybenzoic acid. On shaking up the ethereal solution with water, and adding sodium carbonate to the resulting aqueous solution, sodium carboxytartronate, $C^4H^2Na^2O^7$, separates out as a heavy white crystalline powder. When the filtrate from this precipitate is neutralised with sodium carbonate, glistening yellow scales of sodium dinitrodihydroxyquinone are deposited. The mother-liquor contained oxalic acid and a nitro-product which could not be isolated.

Sodium carboxytartronate is decomposed by water (in which it is almost insoluble) at 60°, carbon dioxide being given off and sodium tartronate formed:



The same change takes place when the dry sodium salt is heated at 100°. Carboxytartronic acid has not been isolated.

Sodium-dinitrodihydroxyquinone, $C^6Na^2H^2O^9 + 2H^2O$, has a strong metallic lustre, and the colour of brass. It dissolves freely in hot water, forming a brown solution. The free acid is very unstable; it crystallises in long greenish-yellow needles, which are freely soluble in water or alcohol, and but sparingly in ether.

On evaporating the ethereal solution of the crude product of the action of nitrous gas on protocatechuic acid, a mixture of picric acid, α -dinitrophenol, and nitrohydroxybenzoic acid is deposited. The mother-liquor contains picric and oxalic acids, and a small quantity of a nitro-product which dissolves in potash with a splendid purple coloration.

The nitrohydroxybenzoic acid was separated from α -dinitrophenol by recrystallisation from cold alcohol, in which the latter is sparingly soluble, and purified by recrystallisation from hot benzene, from which it is deposited on cooling, in compact yellow needles (m. p. 178°), freely soluble in alcohol, ether, and hot water. The hydrochloride of the amidohydroxybenzoic acid, obtained by reduction of the nitro-acid with tin and hydrochloric acid, crystallises in slender needles. The sulphate forms microscopic crystals (Gruber, *Ber.* xii. 514).

HOMOLOGUES OF PROTOCATECHUIC ACID AND ALLIED COMPOUNDS (F. Tiemann, *Ber.* xi. 659).

The compounds containing the common group $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{---} \end{array} > \text{C}^{\text{H}}\text{---C}\equiv$, and therefore derivable from protocatechuic acid, $\begin{array}{c} \text{HO} \\ \diagup \quad \diagdown \\ \text{HO} \end{array} > \text{C}^{\text{H}}\text{---COOH}$, may be arranged in four parallel series, viz.:

1. The *Protocatechuic series proper*, the members of which contain in the side-chain a single carbon-atom $\text{---C}\equiv$.

2. The *α -Homoprotocatechuic series*, the characteristic group of which is the side-chain $\text{---CH}^2\text{---C}\equiv$.

3. The *Hydrocaffeic series*, the members of which contain in the side-chain the group $\text{---CH}^2\text{---CH}^2\text{---C}\equiv$.

4. The *Caffeic series*, containing in the side-chain the group $\text{---CH=CH---C}\equiv$.

The first of the two following tables (p. 1692) exhibits the constitution and melting points of the known acids of these protocatechuic series, from which it will be seen that the melting point of an acid in each homologous series is for the most part lower as the position of the acid in that series is higher; and, on the other hand, that a gradual rise of melting point takes place on passing from the hydrocaffeic to the caffeic series. The second table shows the relations, in constitution and melting point, of the acids of the protocatechuic series proper to the corresponding aldehydes and alcohols, and to the phenols formed from the acids by conversion of the COOH-group into CH³.

The letters *m* and *p* in these tables denote that the radicles to which they are attached are in the *meta* and *para* positions with respect to the carboxyl-group.

Methyl-protocatechuic Acids:

Vanillic acid	$\text{C}^{\text{H}}\text{H}^3(\text{COOH})^1(\text{OCH}^3)^3(\text{OH})^4$
Isovanillic acid	$\text{C}^{\text{H}}\text{H}^3(\text{COOH})^1(\text{OH})^3(\text{OCH}^3)^4$
Veratric acid	$\text{C}^{\text{H}}\text{H}^3(\text{COOH})^1(\text{OCH}^3)^3(\text{OCH}^3)^4$

These acids have already been described (under DIOXYBENZOIC ACIDS, pp. 289-292). The following additional observations on them have been recently published by K. U. Matsumoto (*Ber.* xi. 122).

Isovanillic acid is best prepared by heating veratric acid (2 grams) for five hours at 160°-170° with dilute hydrochloric acid (75 c.c. of a mixture of 1 pt. hydrochloric acid, sp. gr. 1.20, and 2 pts. water), and may be purified by boiling it with acetic acid, and pouring the product into water, whereupon acetisovanillin separates out, while veratric acid remains in solution. The acetyl-compound, boiled with dilute potash-solution, yields pure isovanillic acid. This acid crystallises in shining transparent prisms, like those of vanillic acid, and melts at 250°. It is soluble in alcohol and ether. Its aqueous solutions give no reaction with ferric chloride. The alkaline isovanillates are easily soluble in water, and those of barium, calcium, and magnesium are tolerably soluble salts, crystallising in needles. The lead salt is obtained as a difficultly soluble white crystalline precipitate; the silver salt is also white, and is decomposed by light less rapidly than the vanillate.

The following are the solubilities of the three methylated protocatechuic acids in water:

			Pts. of water,	
			at 14°	at 100°
1 pt. veratric acid	(m. p. 174°-175°)	2100-2150	160-165
1 " vanillic acid	(" 207°)	850-860	39-40
1 " isovanillic acid	(" 250°)	1650-1700	155-160

The methyl and ethyl ethers of these acids were obtained by passing hydrochloric acid gas through a solution of the acid in the respective alcohols.

Methyl Vanillate, $\text{C}^{\text{H}}\text{H}^3(\text{OCH}^3)\text{OH.COOCCH}^3$, crystallises in shining white needles melting at 62°-63°. It boils at 285°-287°, and is not attacked by alkalis at the ordinary temperature.

Methyl Veratrate, $\text{C}^{\text{H}}\text{H}^3(\text{OCH}^3)^2.\text{COOCCH}^3$, is difficultly soluble in water, easily in ether and alcohol, and crystallises from its alcoholic solution in white needles. It melts at 59°-60°, and boils at 300°, is odourless, and not attacked by ammonia or alkalis at the ordinary temperature. This ether may also be prepared by heating potassium hydrate, methyl iodide, and vanillic acid in sealed tubes. The product of the reaction is then shaken up with ether, and the ethereal solution treated with dilute solution of potassium hydrate to remove unaltered vanillic acid.

TABLE I.—Acids.

Protocatechuic series proper	Alpha-homoprotocatechuic series	Hydrocaffeic series	Caffeic series
Protocatechuic acid $C^*H^*(OH)_m(OH)_pCOOH$ M. P. 199°	Alpha-homoprotocatechuic acid $C^*H^*(OH)_m(OH)_pCH_2COOH$ M. P. 127°	Hydrocaffeic acid $C^*H^*(OH)_m(OH)_pCH_2CH_2COOH$ M. P. (?)	Caffeic acid $C^*H^*(OH)_m(OH)_pCH=CHCOOH$ Decomposes without melting at any particular temperature
Vanillic acid $C^*H^*(OCH_3)_m(OH)_pCOOH$ M. P. 207°	Alpha-homovanillic acid $C^*H^*(OCH_3)_m(OH)_pCH_2COOH$ M. P. 142°-143°	Hydrovanillic acid $C^*H^*(OCH_3)_m(OH)_pCH_2CH_2COOH$ M. P. 89°-90°	Ferulic acid $C^*H^*(OCH_3)_m(OH)_pCH=CHCOOH$ M. P. 168°-169°
Isovanillic acid $C^*H^*(OH)_m(OCH_3)_pCOOH$ M. P. 250°	Alpha-homoisovanillic acid unknown	Hydroisovanillic acid $C^*H^*(OH)_m(OCH_3)_pCH_2CH_2COOH$ M. P. 146°	Isoferulic acid $C^*H^*(OH)_m(OCH_3)_pCH=CHCOOH$ M. P. 211°-212°
Veratric acid $C^*H^*(OCH_3)_m(OCH_2)_pCOOH$ M. P. 174°-175°	Alpha-homoveratric acid $C^*H^*(OCH_3)_m(OCH_2)_pCH_2COOH$ M. P. 98°-99°	Hydroveratric acid $C^*H^*(OCH_3)_m(OCH_2)_pCH_2CH_2COOH$ M. P. 99°-97°	Dimethyl-cafeic acid $C^*H^*(OCH_3)_mCH=CHCOOH$ M. P. 180°-181°
Piperonylic acid $C^*H^*(O_mCH_2)_pCOOH$ M. P. 228°			

TABLE II.—Aldehydes, Alcohols, Phenols.

	Protocatechuyl series	Protocatechuyl series	
Homocatechol $C^*H^*(OH)_mCH^*$	Protocatechuyl alcohol unknown	Protocatechuic aldehyde $C^*H^*(OH)_mCOH$ M. P. 186°	Protocatechuic acid $C^*H^*(OH)_mCOOH$ M. P. 199°
Cresol $C^*H^*(OCH_3)_m(OH)_pCH^*$ B. P. 220°	Vanillyl alcohol $C^*H^*(OCH_3)_m(OH)_pCH_2OH$ M. P. 108°-109°	Vanillin $C^*H^*(OCH_3)_m(OH)_pCOH$ M. P. 81°	Vanillic acid $C^*H^*(OCH_3)_m(OH)_pCOOH$ M. P. 207°
Methyl cresol $C^*H^*(OCH_3)_mCH^*$ B. P. 214°-218°	Veratryl alcohol unknown	Veratryl-aldehyde (Methyl-vanillin) $C^*H^*(OCH_3)_pCOH$ M. P. 42°-43°	Veratric acid $C^*H^*(OCH_3)_pCOOH$ M. P. 174°-175°
Eugenol $C^*H^*(OCH_3)_m(OH)_pCH^*$ B. P. 248°	Coniferyl alcohol $C^*H^*(OCH_3)_m(OH)_pCH_2OH$ M. P. 74°-75°	Ferulic aldehyde unknown	Ferulic acid $C^*H^*(OCH_3)_m(OH)_pCH=CHCOOH$ M. P. 168°-169°
Methylene-homocatechol unknown	Piperonyl alcohol $CH^*(O_mCH_2)_pCH_2OH$ M. P. 51°	Piperonal $CH^*(O_mCH_2)_pCH_2COH$ M. P. 37°	Piperonylic acid $CH^*(O_mCH_2)_pCH=CHCOOH$ M. P. 228°

Ethyl Veratrate crystallises in colourless needles, soluble in alcohol and ether, melts at 43° – 44° , and boils at 295° – 296° .

Methyl Nitroveratrate, $C^6H^2(NO^2)(OCH^3)^2CO^2CH^3$, prepared, like the ethyl-compound (p. 290), from nitroveratric acid, is sparingly soluble in water and cold alcohol, but dissolves easily in boiling alcohol and ether, and crystallises in needles melting at 143° – 144° .

Methyl Isonitroveratrate, produced by heating nitrovanillic acid with methyl iodide and potassium hydrate, dissolves sparingly in water, readily in alcohol and ether, and crystallises from dilute alcohol in hard shining needles melting at 127° – 128° . The difference in properties between this and the preceding ether shows that the position of the nitro-group in nitrovanillic acid is different from that which it occupies in nitroveratric acid. The last-described ether yields by saponification isonitroveratric acid, $C^6H^2(NO^2)(OCH^3)^2COOH$, which crystallises in white anhydrous needles melting at 200° – 202° .

Ethyl Amidoveratrate, $C^6H^2(NH^2)(OCH^3)^2CO^2C^2H^5$, is produced by treating the corresponding nitro-ether with tin and hydrochloric acid, and may be separated from the solution of its hydrochloride by dilute soda-ley or ammonia. It crystallises from dilute alcohol in small colourless needles melting at 88° – 89° .

Acetisovanillic acid, $C^6COOH.H.O.C^2H^3O.OCH^3.H^2$, prepared, like acetovanillic acid (p. 290), by digesting isovanillic acid at 100° , and precipitating with water, crystallises from dilute alcohol in shining scales melting at 206° – 207° , very slightly soluble in water, easily soluble in alcohol and ether.

Nitro-acetisovanillic acid, $C^6H^2(NO^2)(O.C^2H^3O)_m(OCH^3)_nCOOH$, prepared like nitro-acetovanillic acid (p. 290), crystallises in shining needles melting at 168° – 169° , sparingly soluble in cold water, more freely in hot water, easily in alcohol and ether. By boiling with alkalis, it is converted into *nitroisovanillic acid*, $C^6H^2(NO^2)(OH)_m(OCH^3)_nCOOH$, which crystallises from hot water in spherical groups of needles melting at 172° – 173° , easily soluble in alcohol and ether.

Bromoveratric acid, $C^6H^2Br(OCH^3)^2COOH$, first obtained, though not pure, by Kölle (vii. 432), may be prepared by adding bromine (rather more than 1 mol.) to a hot aqueous solution of 1 mol. veratric acid. A red resin then separates, and from the liquid decanted therefrom the brominated acid crystallises in colourless needles melting at 183° – 184° . It is nearly insoluble in cold water, slightly soluble in hot water, easily in alcohol and ether. By fusion with potash it yields gallic acid.

The red resin contains dibromodimethylcatechol, or dibromoveratrol, $C^6H^2Br^2(OCH^3)^2$, which may be extracted from it by solution in alcohol, and separates from the alcoholic solution, first as an emulsion, afterwards crystalline. From dilute alcohol it crystallises in hard shining prisms melting at 83° – 84° .

Bromoacetovanillic acid, $C^6H^2Br(OCH^3)(OC^2H^3O)COOH$, is produced, together with bromovanillic acid, by bromination of acetovanillic acid, and crystallises from hot water or dilute alcohol in anhydrous prisms melting at 165° – 167° .

Bromovanillic acid, $C^6H^2Br(OCH^3)(OH)COOH$, obtained by the action of potash-ley on its aceto-derivative, is much more soluble in water than the latter, very soluble in alcohol and ether, and crystallises from hot water with 1 mol. H^2O , which is given off at 100° – 110° . The dehydrated compound melts at 192° – 193° . When heated with methyl iodide and potassium hydrate, it is converted into the methyl-ether of the above-described bromoveratric acid. Hence it appears that—contrary to what takes place with the nitro-group,—the bromine replaces in acetovanillic acid the same hydrogen-atom as in acetoveratric acid.

Caffeic and Ferulic Acids. The following details respecting the preparation and properties of these acids, and some of their derivatives, are given by F. Tiemann a. Nagajosi-Nagai (*Ber.* xi. 658).

Acetovanillin, $C^6H^3(COH)(O.CH^3)(O.C^2H^3O)$, is best prepared by allowing the sodium-compound of vanillin to remain in contact with an ethereal solution of acetic anhydride for some hours. It forms large flat needles which melt at 77° ; it is easily soluble in alcohol and ether, but only sparingly in water.

Acetoferulic acid, $C^6H^3(CH=CH.COOH)(O.CH^3)(O.C^2H^3O)$, is formed by heating either vanillin or the preceding compound with anhydrous sodium acetate and acetic anhydride. It crystallises in slender needles melting at 196° – 197° ; it is readily soluble in alcohol and in ether, but with difficulty in water.

Ferulic acid, $C^6H^3(CH=CH.COOH)(O.CH^3)(OH)$, results from the decomposi-

tion of the preceding compound by sodium hydrate. This synthetic acid crystallises from boiling water in brittle, high refractive prisms, melting at 168° – 169° , which is also the melting point of ferulic acid prepared from *asafoetida* (p. 785). In order, finally, to establish the identity of these products: (1) the latter was heated with acetic anhydride, and found to yield a body identical in all respects with the acetoferulic acid described above; and (2) the acetoferulic acid thus prepared from the 'natural' acid was oxidised by potassium permanganate in acetic acid solution, and found to yield acetovanillin and acetovanillic acid.

In ferulic acid the hydrogen both of the carboxyl-group and of the phenolic hydroxyl is capable of being replaced by metals, so that it yields two classes of salts, of which the primary ammonium and secondary potassium salts have been obtained by Hlasiwetz. Ferulic acid is a hydroxyl-methoxyl-cinnamic acid, and can readily take up two hydrogen-atoms, forming hydroferulic acid.

Hydroferulic acid, $C^mH^p(CH_2.CH_2.COOH)(OCH^m)(OH)$, is easily obtained by the action of reducing agents upon ferulic acid. It crystallises from its aqueous solution in microscopic plates (m. p. 89° – 90°), which are very easily soluble in alcohol, ether, and hot water. Like the preceding it forms two classes of salts.

Dimethylcaffeic acid, $C^mH^p(CH=CH.COOH)(OCH^m)_2$, or *Methylferulic acid*, may be prepared by replacing either the two hydroxyl-groups of caffeic or dioxy-cinnamic acid, or the single hydroxyl-group of ferulic acid with methoxyl, by heating them with potash and methyl iodide in methyl-alcohol solution. Dimethylcaffeic acid crystallises in needles which melt at 180° – 181° . It is monobasic, and forms easily soluble salts with the metals of the alkalis and alkaline earths.

Hydrodimethylcaffeic acid, $C^mH^p(CH_2.CH_2.COOH)(OCH^m)_2$, was obtained by reduction from dimethylcaffeic acid prepared either from ferulic acid or from caffeic acid: the products were identical. This acid crystallises from its aqueous solution in slender needles which melt at 96° – 97° to an oil which solidifies at 60° .

Isoferulic acid, $C^mH^p(CH=CH.COOH)(OH)(OCH^m)$, is formed by heating caffeic acid with methyl iodide and potassium hydrate in quantity less than sufficient for the complete replacement of its hydroxyl. The methyl ethers of isoferulic and dimethylcaffeic acids thereby obtained are easily separated, and the isoferulic acid may be isolated, after saponification, in the form of crystals which melt at 211° – 212° . It forms two classes of salts.

Hydroisoferulic acid, $C^mH^p(CH_2.CH_2.COOH)(OH)(OCH^m)$, is readily formed from the preceding acid by reduction. The pure acid forms slender colourless needles which melt at 146° to an oil which solidifies at 130° .

Synthesis of Caffeic Acid.—By the action of sodium acetate and acetic anhydride on protocathechuic aldehyde, the latter is converted into a diacetocaffeic acid, $C^mH^p(CH=CH.COOH)(OC^mH^pO)(OC^mH^pO)$, identical in every respect with that which is obtained by the action of acetic anhydride on caffeic acid; it crystallises in slender needles, melts at 190° – 191° , and when heated with potash-solution, is readily converted into caffeic acid.

PSEUDAACONITINE and ALLIED BASES (Wright a. Luff, *Chem. Soc. J.* xxxiii. 151; xxxv. 387; *Chem. News*, xxxvii. 67, 215; xxxix. 224).

Pseudaconitine, $C^{36}H^{48}NO^{12}$, is the chief basic constituent of *Aconitum ferox*, but is very difficult to obtain in the pure state, as in the process of extraction it is partly converted, by loss of H^2O , into *apopseudaconitine*, $C^{36}H^{47}NO^{11}$, which adheres to it with great obstinacy, and it is only after a long process of purification (described in the paper above cited) that the pseudaconitine exhibits the composition represented by the formula $C^{36}H^{48}NO^{12}$.

Pure pseudaconitine is more soluble in alcohol and ether than aconitine, and crystallises by slow evaporation from ether, or better from a mixture of ether and light petroleum, in transparent needles and sandy crystals; after rapid evaporation it remains syrupy. In the air-dried state it contains 1 mol. water of crystallisation, which is given off at 80° in a stream of air, and more quickly at 100° , the residue at the same time slightly caking together. At 104° – 105° it melts to a viscid transparent liquid. The solutions of its salts form very sparingly soluble precipitates with potassium-mercuric iodide and bromide, somewhat more soluble precipitates with mercuric chloride, auric chloride, iodised potassium iodide, alkalis and their carbonates, and tannin.

Pseudaconitine may be heated for some time at 105° without sensible alteration of weight, but when it is heated to 135° —or its acetate to 130° – 140° —then dissolved

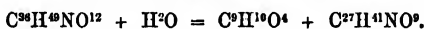
in alcohol, precipitated by sodium carbonate, and taken up by ether, amorphous bases (forming also amorphous salts) are produced, represented by the formulæ $2C^{36}H^{49}NO^{12} - 3H^2O$ and $C^{36}H^{49}NO^{12} - 2H^2O$.

Apopsedaconitine, $C^{36}H^{47}NO^{11}$, is formed by abstraction of water from pseudaconitine under the influence of mineral acids. The action takes place even with very dilute acids and at ordinary temperatures, but is not complete even at 100° ; it is however mainly represented by the equation $C^{36}H^{49}NO^{12} = H^2O + C^{36}H^{47}NO^{11}$, and the apopsedaconitine may be easily separated from the product by supersaturation with sodium carbonate and agitation with ether. This base is very much like pseudaconitine, but somewhat less soluble in alcohol and ether. In the air-dried state it contains 1 mol. H^2O , which is given off at 100° . It forms a well-crystallised *nitrate*, and an *aurochloride*, $C^{36}H^{47}NO^{11} \cdot HCl \cdot AuCl^3$, very much like that of pseudaconitine.

Acetyl-apopsedaconitine, $C^{36}H^{46}(C^2H^3O)NO^{11}$, is formed on heating pseudaconitine at 100° with acetic anhydride or glacial acetic acid, and separated from the product by agitation with ether. It is crystalline, contains in the air-dried state 1 mol. water, forms a well-crystallised *nitrate* and *aurochloride*. By saponification with alkalis it is resolved into acetic and dimethylprotocatechuic acids.

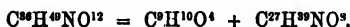
Benzoylapopsedaconitine, $C^{36}H^{46}(C^7H^5O)NO^{11}$, formed in like manner by the action of benzoic anhydride on pseudaconitine, also contains in the air-dried state 1 mol. water of crystallisation, and is altogether very much like the acetylated base.

Pseudaconine, $C^{27}H^{41}NO^9$, is formed, together with dimethylprotocatechuic acid, by heating pseudaconitine at 100° with alcoholic soda-solution:



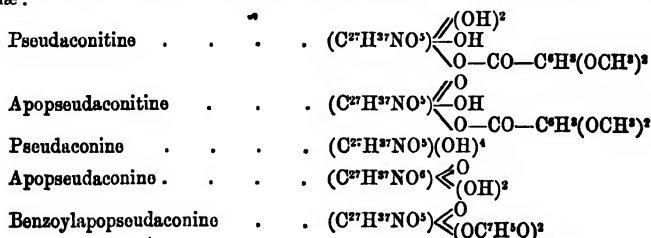
To separate the pseudaconine, the liquid product of the reaction is evaporated to dryness, then acidulated with hydrochloric acid, and shaken with ether; the dimethylprotocatechuic acid thereby dissolved is removed; the residue exhausted with alcohol; the alcohol distilled off; and the pseudaconine dissolved out of the residue by ether, which leaves it on evaporation as a varnish-like but apparently crystallisable mass. It melts at the heat of the water-bath; dissolves readily in water; has a strong alkaline reaction; a bitter but not caustic taste; and is distinguished from pseudaconitine by its greater solubility both in the free state and in combination with acids. It reduces gold and silver salts. Pseudaconine salts are all amorphous.

Apopsedaconine, $C^{27}H^{39}NO^8$, is formed, together with dimethylprotocatechuic acid, by the action of alcoholic soda-solution at 140° on pseudaconitine:



Dibenzoyl-apopsedaconine, $C^{27}H^{37}(OC^7H^5O)^2NO^8$, and the corresponding *diacetyl-derivative*, are obtained by heating pseudaconine with benzoic and acetic anhydride respectively, 1 mol. H^2O being first separated from the pseudaconine and an atom of hydrogen in the residue then replaced by benzoyl or acetyl. Both these bases are amorphous, and form amorphous salts, those of the benzoylated base being nearly insoluble, and those of the acetylated base moderately soluble in water. Both melt at 100° , and decompose at higher temperatures.

The bases above described may be represented by the following constitutional formulæ:



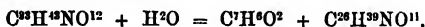
Aconitine, $C^{33}H^{43}NO^{12}$ (Wright & Luff, *Chem. Soc. J.* xxxiii. 318; see also p. 40 of this volume). This is the principal alkaloid of monkshood (*Aconitum Napellus*). It reacts with acids and alkalis in the same manner as pseudaconitine, producing the following bases:

Apoaconitine, $C^{33}H^{41}NO^{11}$, is formed from aconitine by the action of dilute mineral acids or of concentrated tartaric acid (which, however, partly act in the same manner as alkalis, *infra*). It crystallises from ether, melts at 185° – 186° , forms a crystallised

nitrate, and a hydrobromide having the composition $C^{28}H^{40}NO^{11}, HBr + 2\frac{1}{2}H^2O$. This base is probably formed by decomposition of aconitine during the preparation of the latter, and to its admixture may be attributed the very discordant statements which have been made respecting the composition of aconitine.

Acetylaponaconitine, $C^{33}H^{40}(C^2H^3O)NO^{11}$, and *Benzoyl-aponaconitine*, are produced by heating aconitine with acetic and benzoic anhydride respectively, a molecule of water being first removed, and an atom of hydrogen in the residue then replaced by acetyl or benzoyl. Acetylaponaconitine crystallises from ether, melts at 180° – 181° (corr.), and forms amorphous salts. In its preparation the temperature must not be allowed to rise above 100° , as otherwise an amorphous base will be formed.

Aconine, $C^{28}H^{39}NO^{11}$, is formed, together with benzoic acid, by the action of dilute alkalis at ordinary temperatures on aconitine, the conversion being most completely effected by the use of alcoholic soda-solution: the same change is also produced by heating aconitine with water at 140° :

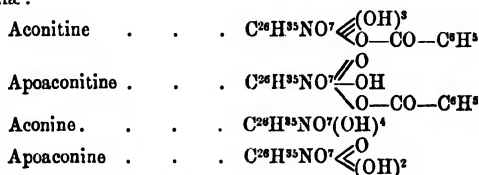


This reaction of aconitine, and the corresponding reaction of pseudaconitine, are analogous to that of cocaine, which yields methyl alcohol, benzoic acid, and ecgonine (vi. 480), and to that of atropine, which yields tropic acid and tropine (vi. 249).

Aconine is easily soluble in water, alcohol, alkalis, and chloroform, but almost insoluble in ether, especially when the ether is free from alcohol. It is amorphous, as are also its salts; melts at 130° ; reduces gold and silver salts, and at the boiling heat also Fehling's solution. The *mercuriodide* has the composition $C^{28}H^{39}NO^{11}, H_2, HgI^2$; the *sulphate* is $7C^{28}H^{39}NO^{11}, H^2SO^4$; the *hydrochloride*, $3C^{28}H^{39}NO^{11}, 2HCl$; these last two salts were probably mixtures. The *aurochloride*, $C^{28}H^{39}NO^{11}, HCl, AuCl^3$, is obtained as a yellow flocculent precipitate on adding gold chloride to the solution of aconine in hydrochloric acid. Aconine heated with benzoic anhydride is converted into benzoylaponaconitine.

Apoaconine, $C^{28}H^{37}NO^{10}$, is formed by abstraction of water from aconine under the influence of dilute acids, e.g. by heating a solution of the hydrochloride to 140° . Its *hydrochloride*, $C^{28}H^{37}NO^{10}, HCl$, is amorphous, soluble in water, not precipitated by alkalis.

The relations between the four bases just described may be represented by the following formulæ:



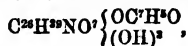
Picraconitine, $C^{31}H^{43}NO^{10}$, is the amorphous and comparatively inert alkaloid occurring, together with aconitine, in *Aconitum Napellus*. It is resolved by alkalis into benzoic acid and *picraconine*, $C^{24}H^{31}NO^9$, and may probably be represented by the formula $C^{24}H^{31}NO^9 \left\{ \begin{array}{l} (OH)^3 \\ O-CO.C^6H^5 \end{array} \right.$

Alkaloid from Japanese Aconite Roots (Wright a. Luff, *Chem. Soc. J.* xxxvi. 387). These roots appear to be different in species both from *A. Napellus* and from *A. ferox*, and are either richer in active ingredients, or else contain a more active alkaloid. To obtain the base, the roots were exhausted with alcohol containing tartaric acid; the extract was evaporated; and the residue, after addition of water and sodium carbonate, was agitated with ether. Repeated treatment with ether, however, failed to dissolve all the alkaloid present, a portion, apparently uncrystallisable, being obstinately retained by the alkaline liquid. The ethereal extract, after purification by shaking with aqueous tartaric acid, and treatment of the crude tartrate solution with soda and fresh ether, gave by spontaneous evaporation crops of crystals, all of which, when purified by fractional crystallisation, yielded on analysis numbers agreeing with the formula $C^{46}H^{66}N^2O^{27}$. As no change in the composition of this body was produced by treatment with hot concentrated tartaric acid, Wright a. Luff conclude that it is a definite compound, and not a mixture of two bases, $C^{32}H^{48}NO^{11}$ and $C^{38}H^{54}NO^{10}$.

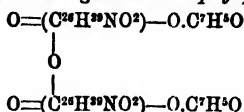
This compound melts at 185° – 186° , and closely resembles aconitine. By saponification it is resolved into benzoic acid and japaconine, $C^{26}H^{48}NO^{11}$, a base which bears a close resemblance to aconine, but forms with benzoic anhydride a tetra- instead

of a di-benzoylated derivative. A tetrabenzoyl-compound is also formed by heating the base $C^{26}H^{22}N^2O^{21}$ with benzoic anhydride.

To explain the constitution of these several bases, Wright a. Luff assume the existence of a base (Japaconitine) represented by the formula



containing H^4 more than aconitine, and constituted like aconitine and pseudaconitine. The base $C^{26}H^{22}N^2O^{21}$ may then be regarded as *triapo-japaconitine*,*



and japaconine as $O=C^{26}H^{22}NO^7(OH)^2$.

All attempts to isolate japaconitine were unsuccessful.

Japanese aconite roots have also been examined by Paul a. Kingzett (*Yearbook of Pharmacy*, 1877, p. 469), who find that the yield of alkaloids from them is much greater than that from *A. Napellus* or *A. ferox*. They obtained a crystalline base, to which they assigned the formula $C^{26}H^{22}NO^6$. As, however, this formula was deduced from the analysis of a very small quantity of substance, and as the base in question formed amorphous salts, Wright is inclined to regard it as identical with pseudaconitine, a view with which Kingzett does not agree.

PSEUDOBUTYLBENZENE ALCOHOL, $C^6H^5.CH^2.CH^2.CHOH.CH^3$. An alcohol formed by the action of nascent hydrogen on acetocinnamone (p. 1152).

PSEUDOBUTYLENE, $CH^3-CH=CH-CH^3$. See BUTYLENES (p. 361).

PSEUDOCUMENE. Unsymmetrical Trimethylbenzene. See MXSITYLENE (p. 1284).

PSEUDO-INDOLE. See INDOLE (p. 1089).

PSEUDOMALACHITE, syn. with Ehlite, $5CuO.P^2O^5.3H^2O$ (p. 705).†

PSEUDOMORPHOSES. A description of the numerous pseudomorphoses of the bed of magnetic iron ore in the Tilly-Foster mine, Putnam County, New York, is given by J. D. Dana (*Sill. Am. J.* [3], viii. 371 and 447; *Jahresb. f. Chem.* 1873, 1284-1292). Pseudomorphs of tin-stone, after orthoclase, from Huel Coates, St. Agnes, Cornwall, are described by J. A. Phillips (*Chem. Soc. J.* xxviii. 684).

On the Microscopical Structure of Pseudomorphs, see Geinitz (*Jahrb. f. Min.* 1876, 449-504; *Chem. Soc. J.* xxxi. 621-700).

PSEUDONITROLES. See PARAFFINS (NITRO-), p. 149.

PSEUDOPHITE. See PENNINE (p. 1498).

PSEUDOPROPYL- or **ISOPROPYL-COMPOUNDS**. See PROPYL-COMPOUNDS (pp. 1676-1679).

PSEUDOPURPURIN. See ANTHRAQUINONES, TRIOXY- (p. 111).

PSEUDOROSANILINE. See ROSANILINE.

PSEUDOROSOLIC ACID. See ROSOLIC ACID.

PSEUDOTHIOCYANOGEN. The orange-yellow precipitate (*Persulphocyanogen*, iv. 381) which Liebig obtained by the action of chlorine or nitric acid on aqueous potassium thiocyanate, is generally represented by the formula $C^2N^2S^2H$. According to W. R. Hodgkinson, however (*Chem. News*, xxxix. 80), its true composition is represented by the empirical formula CNSH, and it is actually a polymeride of thiocyanic acid, $C^2N^2S^2H^2$. Hodgkinson recommends the use of this yellow substance as a pigment, as it is not altered by light either in the moist or in the dry state.

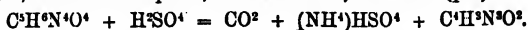
PSEUDOTOLUIDINE. See TOLUIDINE.

PSEUDO-URIC ACID, $C^8H^4N^4O^4$. This acid, which Schlieper a. Baeyer obtained (iv. 744) by the action of potassium cyanate on uramil (dialuramide), is also produced as ammonium salt, with elimination of ammonia, when uramil is heated with an equal weight of urea. On passing carbon dioxide through a solution of the

* Wright a. Luff designate this base as *japaconitine*; but if $C^{26}H^{22}NO^{11}$ is to be called *japaconine*, it is more consistent to give the name of *japaconitine* to the hypothetical base $C^{26}H^{22}NO^{12}$, related to japaconine in the same manner as aconitine to aconine.

† CuO is there misprinted CaO.

resulting ammonium-salt in caustic soda, sodium pseudourate separates out, and from this salt the acid may be obtained by precipitation with hydrochloric acid. Its *barium salt*, $(C^4H^2N^4O^4)^2Ba + 5H^2O$, gives off all its water at 150° . The acid is not attacked by phosphorus oxychloride. Sulphuric acid decomposes it at 150° into carbon dioxide, ammonium sulphate, and xanthine, $C^4H^2N^4O^2$ (q.v.):



Pseudo-uric acid is uric acid plus the elements of water, but all attempts to resolve it into these constituents have hitherto been unsuccessful (Grimaux, *Bull. Soc. Chim.* [2], xxxi. 535).

PSEUDOTRIACETONALKAMINE. See ACETONAMINES (p. 32).

PSEUDOTRIPHENYLMELAMINE, $C^6H^3(C^4H^3)^3N^6$, isomeric with Hofmann's triphenylmelamine (p. 1271), is formed, together with carbon dioxide, hydrogen cyanide, benzonitril, and dibenzoyl-dicyanamide, by heating tribenzoylmelamine in a current of hydrogen. It is best purified by solution in phenol, and precipitation with alcohol, whereupon it separates in shining yellow prisms which do not melt at 360° . Hofmann's triphenylmelamine melts at 162° – 163° (Gerlich, *J. pr. Chem.* [2], xiii. 270).

PSILOMELANES. See MANGANESE-ORES (p. 1263).

PSITTACINITE. A hydrated vanadate of lead from mines in the Silver Star District, Montana. See VANADIUM MINERALS.

PUCHERITE. Small brown crystals, $OP.\infty P$, identical in form and composition with native pucherite (vii. 1026), are obtained by evaporating a mixture of bismuth nitrate and vanadium chloride in the exsiccator over sulphuric acid (Frenzel, *Jahrb. f. Min.* 1875, 680).

PURPLE OF THE ANCIENTS (Schunck, *Chem. Soc. J.* xxxv. 589). This colour, which was extracted by the ancients from various kinds of shell-fish, and applied to the dyeing of linen and woollen fabrics, has from time to time excited a considerable amount of interest. Cole, of Bristol (*Phil. Trans.* 1685), discovered on the coasts of Somersetshire and South Wales a shell-fish which yielded a purple dye. A similar species (*Purpura Lapillus*) was discovered by Réaumur in 1710; Duhamel in 1736, and Bancroft in 1803, also worked at the subject. Their results may be summarised as follows:—1. The colour-producing secretion resembles pus, and is contained in a small whitish cyst under the shell close to the head of the animal. This pus-like matter, when applied to white linen and exposed to sunlight, changes from yellow, through light green, dark green, and blue, to purplish-red or crimson, a strong odour resembling garlic or assafœtida being at the same time evolved. Daylight is essential; the secretion if kept in the dark remains unchanged for years, and then becomes coloured on exposure to light. The change is not promoted by heat, but proceeds in a vacuum or in hydrogen or nitrogen gas. The colour resists the action of soap, alkalis and most acids; it is destroyed by nitric acid and chlorine. A. and G. de Negri (*Ber.* ix. 84) have recently obtained two colouring matters from a species of murex; one is blue, and presents the characters of indigotin; the other is red, but its nature is not exactly known.

Schunck has made many experiments with *Purpura Lapillus*, which he obtained on rocks at low water near Hastings, live animals alone being used. The pale yellow secretion turns purple when exposed to light, without being applied to linen. Boiling does not hinder the production of the colour. The chromogen can be completely extracted by alcohol and ether from the pounded cysts, a golden-yellow solution being obtained, which becomes purple on exposure to light, and a purple powder being ultimately precipitated, which is granular and crystalline. Hydrochloric acid produces a decomposition somewhat similar to that effected by sunlight, a purple colour being formed. The cysts or veins from 400 animals, yielded on exposure to sunlight 7 mgs. of the purplish powder. It was insoluble in water, alcohol, and ether; slightly soluble in boiling benzene and boiling glacial acetic acid; easily soluble in boiling aniline, the solution giving a broad absorption-band between C and D. Heated between watch-glasses, it yielded a sublimate of crystals with metallic lustre showing at their edges a deep indigo-blue colour. The colouring matter dissolves in strong sulphuric acid to a purplish solution, showing a band between D and E. From these reactions it is inferred that the colouring matter belongs to an unknown member of the indigo-blue group. Schunck proposes to call it *Punicin*. The liquid from which the action of sunlight had precipitated the purple powder did not contain glucose.

PURPUREO-COBALT COMPOUNDS. See COBALT-AMMONIA COMPOUNDS (p. 546).

PURPURIN. See ANTHRAQUINONES (TRIOXY-) (p. 109).

PURPUGALLIN. A substance produced, according to H. Struve, by the slow oxidation of pyrogallol in contact with lead peroxide, gum-arabic, malt-extract, grape-juice, blood-pigment, or saliva (vii. 1029, 1030).

PURPUROXANTHIN. See ANTHRAQUINONES (DIOXY-) (p. 104).

PYRAMARIC ACID, $C^{16}H^{14}O^2$. An acid formed, together with benzoic acid, by the action of heat on amaric acid, $C^{46}H^{42}O^6$, in presence of free alkali (p. 1128).

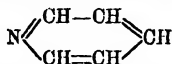
PYRENE, $C^{16}H^{10}$ (vii. 1027). This hydrocarbon crystallises in monoclinic prisms, melts at 148° – 149° , and forms a picric acid compound which melts at 122° . Mononitropyrene melts at 149.5° – 150.5° (Fittig, *Ber.* x. 2143).

PYRETHRUM. On the insect-powders prepared from various species of *Pyrethrum*, see p. 1091. J. de Bollesmo obtained from *Pyrethrum carneum*, which is an ingredient of most of these powders, a volatile non-poisonous oil, and a crystalline body which exhibits the poisonous properties of the plant, and is probably an alkaloid (*Pharm. J. Trans.* [3], vii. 172). R. Buchheim, by evaporating to dryness the alcoholic extract of *Radix pyrethri*, and exhausting the residue with ether, obtained a crystalline substance, *pyrethrin*, which melted at the heat of the body, and was resolved by alcoholic potash into pyrethic acid and piperidine. Pyrethrin occurs also in *Herba spilanthis* (*N. Rep. Pharm.* xxv. 335).

PYRIDINE-BASES, $C^8H^{2a-3}N$. The following bases of this series are known:

	B. p.		B. p.
Pyridine, C^8H^5N	117°	Parvoline, $C^9H^{13}N$	188°
Picoline, C^8H^7N	133	Coridine, $C^{10}H^{15}N$	211
Lutidine, C^8H^9N	154	Rubidine, $C^{11}H^{17}N$	230
Colli-line, $C^8H^{11}N$	179	Viridine, $C^{12}H^{19}N$	251

Pyridine, the lowest member of the series, may be regarded as benzene having one of its CH-groups replaced by nitrogen, and represented by the formula



The other members, derived from it by substitution of CH^3 , C^2H^3 , &c., for one or more of the hydrogen-atoms, admit of isomeric modifications depending on the orientation of the substituted radicles. Picoline or methyl-pyridine, C^8H^7N (CH^3N), admits of three such modifications, which are actually known; the higher members, however, are at present known in one modification only, or perhaps as mixtures of several.

The Heats of Formation of some of these bases have been determined by Ramsay (*Chem. Soc. J.* xxxv. 696) with the following results:

	Gram-degrees		Gram-degrees
Pyridine	7117	Lutidine	7184
Picoline	5753	Dipicoline	8084

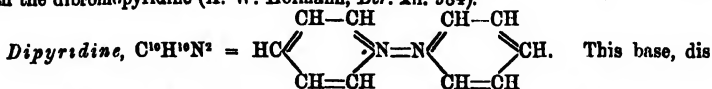
On their volumes at the respective boiling points, see Ramsay (*ibid.* 472).

Physiological action.—Pyridine, picoline, lutidine, and their salts, exert a soporific action on the animal organism; their methiodides strongly excite the brain and paralyse the extremities. A similar but more energetic action is exerted by their ethyl and allyl derivatives; also by dipyridine and dipicoline. The iodalkyl-compounds (methiodides, ethochlorides, &c.) of the last two bases are strong poisons. Methyl pyridine-carboxylate scarcely acts on the organism; the corresponding ammonium salt gives rise to symptoms resembling epileptic fits (Ramsay, *Phil. Mag.* [5], iv. 241). According to Kondrick a. Dewar (*Proc. Roy. Soc.* xxii. 432, xxiii. 290), the several members of the pyridine series differ from one another in their physiological action, not in kind, but only in degree, but the members of the quinoline series, $C^8H^{2a-11}N$ (quinoline, C^8H^7N ; lepidine, C^8H^9N , &c.), exhibit differences in kind, as well as in degree, in their physiological action.

Pyridine, C^8H^5N , is formed by distilling a salt of pyridine-carboxylic (nicotinic) acid with lime, $C^8H^4N(CO^2H) = CO^2 + C^8H^5N$ (Weidel, *Liebigs Annalen*, clxv. 238; Laiblin, *Ber.* x. 2136); also by distilling the calcium salt of pyridine-dicarboxylic acid (cinchomeronic acid, p. 484), $C^8H^4N(CO^2H)^2 = 2CO^2 + C^8H^5N$.

Dibromopyridine, $C^8H^3Br^2N$, is formed on heating to 200° a mixture of pyridine hydrochloride and bromine, or the orange-coloured precipitate formed on adding bromine to a solution of pyridine hydrochloride, and separates in needle-shaped crystals soluble in ether and in strong hydrochloric acid, precipitated from the acid solution by

water. It melts at 109° , and begins to sublime at 100° . It is not acted upon by baryta-water, ammonia, alcoholic potash, nitric acid, sulphuric acid, or potassium permanganate. *Monobromopyridine* (b. p. 170°) appears to be formed simultaneously with the dibromopyridine (A. W. Hofmann, *Ber.* xii. 984).



covered by Anderson (vi. 977), is obtained, together with other products, by the action of sodium on pyridine. He found its vapour-density to be 5.92; Ramsay (*Phil. Mag.* [5], iv. 241), working with Victor Meyer's apparatus, finds it to be 5.36; the formula $\text{C}^{10}\text{H}^{10}\text{N}^2$ requires 5.46.

Isodipyridine, $\text{C}^{10}\text{H}^{10}\text{N}^2$, obtained by fractionation from the mother-liquors of the crystalline dipyridine, is a yellow oil, which does not solidify in a mixture of snow and salt, even on addition of crystals of dipyridine. Sp. gr. 1.08. Vapour-density by two determinations, 5.70 and 5.79. It is sparingly soluble in water, but mixes in all proportions with alcohol and ether. Its *hydrochloride* forms hard white crystals; the *platinochloride* is a yellow crystalline precipitate. The *methiodide* is a brilliant scarlet powder, insoluble in absolute alcohol and ether, slightly soluble in aqueous alcohol, freely in water, forming a nearly colourless solution. The *methochloride* is a syrupy liquid, giving with platinic chloride a precipitate of the double salt $\text{C}^{10}\text{H}^{10}\text{N}^2 \cdot 2\text{CH}^3\text{Cl} \cdot \text{PtCl}_2$ (Ramsay, *Chem. Soc. J.* xxxvi. 264).

Picoline, $\text{C}^8\text{H}^7\text{N} = \text{C}^8\text{H}^6(\text{CH}^3)\text{N}$. This base, as already observed, admits of three isomeric modifications, according as the CH^3 -group is placed in the ortho-, meta-, or para-position with regard to the nitrogen-atom of the pyridine-molecule. The basic oil hitherto known as picoline, extracted from coal-tar naphtha, bone-oil, &c., is a mixture of two of these modifications (α and β), and a third modification (γ) is formed by the distillation of acrolein-ammonia and by heating allyl tribromide with ammonia (Baeyer, vi. 944; vii. 981).

The two modifications obtained by the dry distillation of vegetable and animal substances cannot be separated by fractional distillation, but their separation may be effected by means of the different solubilities of their platinochlorides. The following description of their properties is given by Weidel (*Ber.* xii. 2008).

α -Picoline, obtained from the less soluble of the two platinum salts, is optically inactive, boils at 134° (uncorr.), and is converted by oxidation into picolinic acid. Its platinochloride, $(\text{C}^8\text{H}^6\text{N}, \text{HCl})^2\text{PtCl}_4$, separates from a moderately concentrated slightly acid solution in large, yellow, faintly lustrous monoclinic tablets containing 1 mol. H^2O . Ratio of secondary axes $a : b = 1.0548$. Angle $ac = 102^{\circ} 6'$. Observed faces, 0P , ∞P . From a solution strongly acidulated with hydrochloric acid, on the other hand, the salt separates in large highly lustrous roseate anhydrous prisms also monoclinic, $a : b : c = 0.9185 : 1 : 0.9279$; $ac = 116^{\circ} 10'$. Observed faces ∞P , 0P , $4\text{P}2$.

β -Picoline, obtained from the more soluble of the two platinum salts, is slightly laevogyrate, boils at 140° , and is converted by oxidation into nicotinic acid (p. 1703). It is less soluble in water than α -picoline. Its platinochloride separates from a moderately concentrated solution by slow evaporation in large highly lustrous crystalline grains having the colour of potassium dichromate; by rapid crystallisation from strong solutions it is obtained in needles. The crystals contain 1 mol. H^2O , and belong to the orthorhombic system; $a : b : c = 0.9560 : 1 : 0.6226$. Observed faces P , ∞P , $\infty\text{P}\infty$.

γ -Picoline also yields a platinochloride which crystallises with 1 mol. water. The crystals, according to Groth's measurements (*Liebig's Annalen*, clv. 281), are monoclinic, having the axial ratio $a : b : c = 0.9089 : 1 : 0.6641$, and the axial angle $ac = 81^{\circ} 7'$.

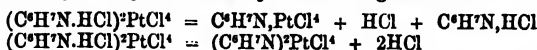
A considerable number of salts prepared from the mixture of α - and β -picoline, hitherto known as 'picoline,' and so designated, for simplicity, in the following descriptions, have been examined by W. Ramsay (*Phil. Mag.* [5], ii. 269; iv. 241; vi. 19). The *hydrochloride*, when purified by distillation, is a white deliquescent salt melting at 160° . It appears to absorb chlorine, but is not attacked thereby even at high temperatures. The *hydrobromide*, on the other hand, in aqueous solution, unites readily with a molecule of bromine, forming the compound $\text{C}^8\text{H}^7\text{N} \cdot \text{Br}_2 \cdot \text{HBr}$, which is still more readily formed by heating a concentrated solution of the hydrobromide with bromine for an hour at 190° . It crystallises from water in yellow needles which melt and give off bromine at about 85° . This dibromide is resolved by boiling with water into bromine and picoline hydrobromide, and the same decomposition is produced by alkalis, but, on acidulating the alkaline solution, the dibromide appears to be reproduced. Bromine does not exert a substituting action on picoline hydro-

bromide, even when heated with it for a week at 180°. When a mixture of picoline and very strong *hydriodic acid* is first evaporated down and then distilled, a sudden rise of temperature takes place, the mass turns brown and viscid, and the compound C^6H^7N, I^2, HI separates in brown needles which melt at 79°, dissolve with decomposition in ether and in alcohol, and, in contact with water, are converted into a dark brown liquid. This compound is not soluble in carbon disulphide.

Picoline dibromide, $C^6H^7NBr_2$, is formed by treating picoline dissolved in chloroform with bromine, and is obtained in small needles on evaporating the chloroform in a vacuum. A *chloriodide*, C^6H^7N, HI , prepared in like manner with picoline and iodine monochloride, forms long yellow needles. These two compounds are resolved by alkalis into picoline and the respective halogens; the dibromide, when heated, decomposes and is converted into a resin.

The compound of picoline with *mercuric chloride*, $C^6H^7N, HgCl_2$, crystallises from water in needles, from alcohol in plates; it is not attacked by chlorine.

Picoline platinochloride, heated with water in a sealed tube for some days at 170°, yields two compounds which can be separated from one another by their different degrees of solubility. They are formed by the following reactions:



The compound $(C^6H^7N)^2PtCl^4$ is a bright yellow powder moderately soluble in water; $C^6H^7N, PtCl^4$ is an insoluble substance of a dirty yellowish-green colour. Neither of these bodies evolves picoline when boiled with caustic alkalis.

Picoline platinosocyanide, $(C^6H^7N, HCN)^2, Pt(CN)^2 + 4H^2O$, forms yellow transparent crystals; from a hot solution it separates in needles containing 5 mols. water. It dissolves in 83 pts. water at 10°. When picoline is left in contact with *hydroferrocyanic acid*, a blue precipitate is formed, together with crystals, probably consisting of *picoline ferrocyanide*. Picoline hydrochloride and *silver cyanate* react at ordinary temperatures with formation of silver chloride; and the liquid, when left to evaporate over sulphuric acid, deposits crystals which are resolved by water into picoline and a gas, and when heated alone split up into picoline, ammonia, and cyanamide.

Picoline methiodide, C^6H^7N, CH^3I , prepared by direct combination of methyl iodide with picoline, is a slightly deliquescent salt which crystallises from alcohol in long white needles, melting at 226.5°–227°. It unites with *iodine*, forming the compound C^6H^7N, I^2, CH^3I , which crystallises in bluish-black feathery plates melting at 129°, soluble in alcohol and in ether, insoluble in carbon sulphide and in water. The *methochloride*, prepared by the action of silver chloride on the methiodide, is deliquescent, and crystallises from alcohol in needles. Its platinum salt, $(C^6H^7N, CH^3Cl)^2PtCl^4$, crystallises in small cubes. The *methonitrate*, C^6H^7N, CH^3NO^3 , obtained from the methiodide with silver nitrate, forms transparent prisms sometimes an inch long. The *methydroxide*, prepared by adding silver oxide to the methiodide, decomposes when evaporated to dryness, leaving a red residue having a putrid odour. The *ethylenobromide*, $(C^6H^7N)^2C^2H^4Br^2$, crystallises with difficulty in small prisms melting at 276°. The corresponding *chloride* crystallises from alcohol in small needles.

The compounds of picoline with *allyl chloride*, *iodide*, &c. are all syrups, except the platinochloride, $(C^6H^7N, C^3H^5Cl)^2PtCl^4$.

Picoline acetochloride, C^6H^7N, C^2H^3OCl , is formed on mixing the solutions of picoline and acetyl chloride in chloroform, the liquid turning first green, then red, and finally red-brown, and yielding the compound, on evaporation in a vacuum, in brown, very deliquescent crystals, which are decomposed by water into picoline hydrochloride and acetic acid. The *benzochloride* exhibits similar properties.

Picoline tartrate, $(C^6H^7N)^2C^4H^4O^6$, crystallises in white needles, smelling faintly of picoline. The *citrate* is a syrup. The *phosphate* is a crystalline mass which rapidly absorbs water. The *chlorate* forms thin diamond-shaped crystals. Picoline does not combine with acetic, formic, or chromic acid.

Dipicoline, $C^{12}H^{14}N^2$, is formed by the action of sodium on picoline, and may be separated from the product by fractional distillation in a vacuum, under which circumstances it boils at 165°–175°. It is a heavy oil, having a peculiar basic odour, a density of 1.12, boiling under ordinary pressure at 310°–320°, and slightly volatile with vapour of water. Most of its salts show but little tendency to crystallise, but the platinochloride, $C^{12}H^{14}N^2, 2HCl, PtCl^4$, is a yellow crystalline powder. The *methiodide*, $C^{12}H^{14}N^2, 2CH^3I$, is a bright yellow powder, almost insoluble in alcohol and ether, but readily soluble in water, giving a colourless solution. The *metho-*

chloride is a white crystalline salt. The *methylplatinochloride*, $C^2H^{11}N^2 \cdot 2CH^3Cl \cdot PtCl_4$, is deposited from water in yellow crystals. Iodine combines with the methiodide, forming brown scales, insoluble in carbon bisulphide, and having the composition $C^2H^{11}N^2 \cdot 2CH^3I \cdot I_2$. With *bromine water*, dipicoline gives a bulky buff-coloured precipitate of the compound $C^2H^{10}BrN^2 \cdot 2HBr$. On oxidation with potassium permanganate, dipicoline yields a mixture of acids, which when heated evolve the smell of the polymerised bases; hence it is probable that a polymeride of pyridine-dicarboxylic acid is produced.

On *Lutidine*, C^6H^8N , see iii. 737; vii. 758. On *Collidine*, $C^8H^{11}N$, i. 1082, vii. 378; viii. 552.

Parvoline, $C^8H^{13}N$ (b. p. 188°), was discovered by C. Greville Williams amongst the volatile bases obtained by the dry distillation of the bituminous shale of Dorsetshire (*Chem. Soc. J.* vii. 97). It occurs also, together with the other bases of the series, in tobacco-smoke (Vohl a. Eulenberg, *Arch. Pharm.* [2], cxlvii. 130).

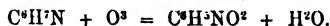
Coridine, $C^{10}H^{15}N$, was discovered by G. Thenius (*Chem. Centr.* 1862, 53) among the bases obtained by distillation of coal-tar. It is a colourless transparent liquid, having a faint odour much like that of new leather. It boils at 211°, and has a density of 0.974. It blues reddened litmus-paper, dissolves sparingly in water, mixes in all proportions with alcohol, ether, and essential oils. Its solutions in acids, when evaporated over the water-bath, yield gummy masses which solidify in the crystalline state when left over calcium chloride. The base itself does not solidify at -17°. The hydrochloric acid solution gives, with mercuric chloride, a white precipitate which is deposited from the warm liquid as a heavy oil, solidifying at low temperatures, and becoming liquid again at 28°; from hot water it crystallises on cooling in white needles. The *platinochloride*, $(C^{10}H^{15}N \cdot HCl)^2 \cdot PtCl_4$, is a dark orange-coloured precipitate, sparingly soluble in water, alcohol, and ether; the *aurochloride* is dark yellow. The base precipitates alumina, chromic oxide and ferric oxide, but not baryta or magnesia. With chloride of lime it produces a yellowish-red colour, which disappears on addition of an acid; a deal-shaving moistened with hydrochloric acid is coloured by it in a similar way.

On *Rubidine*, $C^{11}H^{17}N$ (b. p. 230°), see v. 127. On *Viridine*, $C^{12}H^{19}N$ (b. p. 251°), see v. 1003; vii. 1161.

PYRIDINE-CARBOXYLIC ACIDS. Acids are known derived from pyridine by the substitution of one, two, and three carboxyl-groups for hydrogen.

Pyridine-monocarboxylic Acids, $C^6H^5NO^2 = C^6H^4N \cdot COOH$. The constitutional formula of pyridine (p. 1699) shows that three of these acids are possible, the nitrogen and carboxyl occupying the relative positions 1 : 2, 1 : 3, and 1 : 4. They are all known, but the orientation of the carboxyl-group in each has not been determined. One of these acids, *picolinic acid*, is obtained by oxidation of α -picoline; another, *nicotinic acid*, by oxidation of nicotine and of β -picoline, and the third by the dry distillation of pyridine-tricarboxylic acid.

(1). *Picolinic acid* (H. Weidel, *Ber.* xii. 1994).—This acid is formed, together with nicotinic acid, by the action of potassium permanganate on the mixture of α - and β -picoline (b. p. 133°–139°) obtained by distillation of animal tar (p. 1700):



The two acids are separated by the difference of solubility of their copper salts, the less soluble salt, when decomposed by hydrogen sulphide, yielding picolinic acid, the more soluble yielding nicotinic acid.

Picolinic acid crystallises in white slender apparently prismatic needles, dissolves easily in water and alcohol, but is nearly insoluble in ether, benzene, chloroform, and carbon sulphide. It is scentless and has an acid taste, with bitter after-taste. It volatilises partially below 100°, melts at 134.5°–136°, then sublimes in highly lustrous needles, and decomposes at a higher temperature, emitting a pungent odour. Its aqueous solution is not precipitated either by normal or by basic acetate of lead, but yields a white gummy precipitate with *silver nitrate*. A moderately dilute solution of the acid or of one of its salts yields with *copper salts* a precipitate consisting of shining needles and laminae of a splendid violet-blue colour, a reaction which may be used for the recognition of the acid. Solutions of picolinic acid are coloured faintly yellow by ferrous sulphate.

Potassium picolinate forms small extremely deliquescent needles and scales; its solution when agitated froths like soapy water. The *ammonium salt* is very soluble, and crystallises by spontaneous evaporation in large colourless triclinic plates having a strong vitreous lustre. The *calcium salt*, $(C^6H^4N \cdot COO)^2Ca + 1\frac{1}{2}H^2O$, is obtained by adding calcium carbonate to a boiling dilute solution of the acid, and evaporating the

filtrate, in tufts of white needles having a faint silky lustre,—or by decomposing the ammonium salt with calcium chloride, whereupon it separates in large efflorescent, apparently prismatic crystals. The water of crystallisation is given off at 160° . The *barium salt*, $(C^6H^4NO^2)^2Ba + H^2O$, prepared like the calcium salt, is much less soluble, and separates from the solution on evaporation in microscopic hard sandy prismatic crystals, which give off their water at 160° . By dry distillation it yields a mixture of pyridine and dipyrindine. The *magnesium salt*, $(C^6H^4NO^2)^2Mg + 2H^2O$, obtained by saturation, crystallises on evaporation in hard shining monoclinic prisms, $a : b : c = 1.1368 : 1 : 0.8590$; angle $ac = 73^{\circ} 52'$. Observed faces, OP , $\infty P \infty$, $R \infty$, ∞P . The water of crystallisation is given off at 140° . The *cadmium salt*, $(C^6H^4NO^2)^2Cd$ (at 120°), obtained in like manner, forms an aggregate of small shining crystalline plates, having a saccharine taste. The *copper salt*, $(C^6H^4NO^2)^2Ca$, is obtained either by decomposing a soluble picolinate with cupric acetate, or by saturating a boiling hot solution of the acid with cupric carbonate, and is deposited on cooling in needles having a blue-violet colour and metallic lustre.

Picolinic acid likewise unites with strong mineral acids, and with the chlorides of gold and platinum. The *hydrochloride*, $C^6H^4NO^2.HCl$, separates on evaporation over sulphuric acid in large colourless highly lustrous orthorhombic prisms. The *platinichloride*, $(C^6H^4NO^2.HCl)^2.PtCl^1 + 2H^2O$, crystallises in monoclinic prisms.

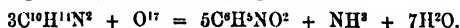
Calcium picolinate, distilled with quick-lime, yields a mixture of pyridine and dipyrindine, the former passing over between 115° and 116° , the latter between 165° and 185° : $C^6H^4NO^2 = CO^2 + C^5H^3N$. Picolinic acid is also resolved into pyridine and carbon dioxide by heating with strong alcoholic potash in a sealed tube at 240° for several hours.

When a solution of sodium picolinate is heated with *sodium-amalgam*, ammonia is given off, and a non-azotised acid is formed, having the composition of hydroxysorbic acid, $C^6H^4O^3$:



This acid crystallises in colourless needles which are extremely deliquescent, very soluble in water, almost insoluble in alcohol, and melt at about 85° . It reduces an alkaline cupric solution. Its barium, calcium, and cadmium salts are amorphous.

(2). *Nicotinic acid*, produced, as above mentioned, by oxidation of the mixture of α - and β -picoline with permanganate, is also formed by oxidation of nicotine. Huber obtained it by oxidising nicotine with chromic acid mixture (vi. 866); Laiblin, by the action of potassium permanganate on the same alkaloid (p. 1392). Weidel in 1872 (*Liebig's Annalen*, clxv. 328), by oxidising nicotine with nitric acid, obtained an acid to which he assigned the formula $C^6H^4N^2O^3$; but his more recent experiments have shown that its true formula is $C^6H^4NO^2$, according to which its formation from nicotine may perhaps be represented by the equation:



For the description of its salts see p. 1392.

Like picolinic acid, it unites with acids as well as with bases. The *hydrochloride*, $C^6H^4NO^2.HCl$, crystallises in monoclinic prisms, in which $a : b = 1.0619$, and the angle $\omega = 80^{\circ} 37'$. Observed faces, OP , $\infty P \infty$, $\infty R \infty$, ∞P . They are very permanent, whereas the crystals of picolinic acid hydrochloride quickly become turbid and opaque.

Nicotinic acid, like picolinic acid, is resolved, by the dry distillation of its calcium salt, into carbon dioxide and pyridine, and when subjected to the action of sodium-amalgam yields an acid apparently identical with the hydroxysorbic acid obtained from picolinic acid.

The points of difference between the two acids may be more plainly seen in the following table (p. 1704).

3. A third pyridine-monocarboxylic acid is obtained by the action of heat on pyridine-tricarboxylic acid: $C^6H^2N(COOH)^3 = 2CO^2 + C^6H^2NO^2$. When this latter acid is cautiously heated to the melting point, carbon dioxide escapes, together with small quantities of other gases, and the fused mass contains a mixture of acids, from which, by repeated crystallisation from water, a pyridine-monocarboxylic acid may be isolated in well-defined granular crystals, while a mixture of mono- and dicarboxylic acids remains in solution.

This pyridine-monocarboxylic acid melts at 305° in closed tubes, volatilises completely under ordinary pressure without previous fusion, and sublimes in fine tabular crystals. Mixed in aqueous solution with cupric acetate and warmed, it yields a green copper salt (Skraup, *Ber.* xii. 2331).

The same acid is also produced, according to Hoogewerff a. van Dorp, who name it *pyrocinchomeronic acid*, by the action of heat on the pyridine-dicarboxylic acid pro-

duced by oxidation of coal-tar quinoline. On heating this dicarboxylic acid in small retorts as long as carbon dioxide continued to escape, and then distilling, a solid distillate was obtained which, when recrystallised from a large quantity of water, yielded the monocarboxylic acid in modular crystals which did not fuse at 275° . The pyridine-monocarboxylic acid thus obtained dissolves sparingly in water, very sparingly in ether and in benzene; its aqueous solution gives no reaction with ferrous sulphate. Its *hydrochloride*, $C^5H^4NO^2.HCl$, forms large shining crystals. The *platinochloride*, $(C^5H^4NO^2.HCl)^2PtCl^4 + 2H^2O$, forms fine red crystals which are very much like those of the corresponding salt of nicotinic acid, and give off their water at 110° – 115° . The mother-liquor of this acid appeared to contain nicotinic acid.

Characters of Pyridine-monocarboxylic acids.

	Picolinic acid	Nicotinic acid
Crystalline form.	Slender, shining anhydrous needles.	Dull anhydrous needles.
Melting point.	134.6° – 136°	228°
Reaction with { Water. Lead acetate. Ammoniacal lead acetate. Copper acetate.	Easily soluble in water, cold or hot. No precipitate. No precipitate. Throws down from a solution of the acid or its salts, after a short time, violet, metallic lustrous laminae, soluble in water on boiling.	Sparingly in cold, easily in warm water. No precipitate. White crystalline precipitate. Light blue-green precipitate, not soluble even in large quantities of water.
„ with Silver nitrate.	White gummy precipitate.	White precipitate.
Crystalline form of ammonium salt.	Triclinic: $a : b : c = 0.9556 : 1 : 0.987$. Always crystallises in large fine tablets.	Obtained only in small lustreless needles, not admitting of measurement.
Crystalline form of calcium salt.	Small shining, unmeasurable needles, or larger prismatic crystals, which soon become turbid.	Monoclinic.
Crystalline form of magnesium salt.	Monoclinic: $a : b : c = 1.1368 : 1 : 0.859$.	Prismatic needles, not admitting of measurement.
Crystalline form of hydrochloride.	Orthorhombic: $a : b : c = 1 : 0.8093 : 0.5635$. The crystals become turbid in a few minutes after removal from the liquid.	Monoclinic: $a : b : c = 1.0619 : 1$. Crystals quite unalterable.
Crystalline form of platinochloride.	Monoclinic: $a : b : c = 1.4468 : 1 : 2.0404$.	Monoclinic: $a : b : c = 1.6233 : 1 : 1.8251$.
Sp. gr. of platinochloride.	2.0672	2.1987

Pyridine-dicarboxylic Acid, $C^5H^4NO^4 = C^5H^3N(COOH)^2$. *Dicarboxypyridenic acid*.—Six modifications of this acid are possible, having the two carboxyl-groups in the following positions [N in 1]:



Five of these acids are known, but the relative positions of the two CO^2H -groups in them have not been determined. Dewar in 1871 (*Chem. News*, xxiii. 18), by oxidising picoline (most probably containing lutidine) with potassium permanganate, obtained an acid of this composition, which crystallised in colourless laminae resembling naphthalene, melted at 210° , and was resolved, at a higher temperature, or by distillation with soda-lime, into CO^2 and pyridine; and two other modifications have been discovered by Ramsay (*Phil. Mag.* [5], iv. 241; vi. 19), who obtained them in a similar manner by the oxidation of lutidine. These two modifications are distinguished as β and γ , Dewar's acid as α .

The general method of preparing these acids is as follows: 25 grams of the base are boiled in a tinned iron vessel connected with an inverted condenser, with 250 grams

of potassium permanganate, and 4 litres of water. When the permanganate has lost its colour, the liquid is distilled, to recover unoxidised base, and the distillate is used instead of water in the next preparation. The potassium salts are then evaporated to dryness, and exhausted with absolute alcohol in an apparatus by which the same alcohol is used over and over again. The salts soluble in alcohol are then dissolved in water, and fractionally precipitated with lead nitrate; the lead salt is decomposed by sulphuretted hydrogen, the lead sulphide removed by filtration, and the filtrate evaporated.

The α -acid, obtained in this way from picoline, separated first in long hair-like needles; on recrystallisation from hot water, it was deposited in plates resembling crystals of naphthalene, and these, on standing in their mother-liquor for some time, changed to short thick prisms. It has a sweet taste but no smell, is more soluble in alcohol than in water, and dissolves also in ether.

The β - and γ -acids were obtained in a similar manner, together with the α -acid, by oxidation of lutidine, and were separated by fractional crystallisation, the β -acid, which is but slightly soluble, separating out first from aqueous solution, as a white crystalline powder, while the γ -acid remained in the mother-liquor.

The table on p. 1706 exhibits a comparative view of the properties of these three acids and of their salts.

A fourth pyridine-dicarboxylic acid is cinchomeronic acid, which Weidel obtained by oxidising cinchonine with nitric acid, and to which he originally assigned the formula $C^{11}H^8N^2O^6$ (p. 483). Later experiments by Weidel and Schmidt (*Ber.* xii. 1146), have shown, however, that it has the composition $C^7H^4NO^4$, and is resolved by distillation into pyridine and CO_2 , and is therefore a pyridine-dicarboxylic acid.

Cinchonine and cinchonidine, when oxidised by nitric acid, yield cinchoninic acid, $C^{10}H^7NO^2$, and quinolic acid, $C^8H^5NO^2$, as well as cinchomeronic acid, but quinine, when oxidised in the same manner, yields cinchomeronic acid as sole product.

Cinchomeronic acid crystallises in white prismatic needles, which melt at 250° , with partial decomposition, and dissolve but very sparingly in boiling water. It is a bibasic acid, and forms two classes of salts. *Sodium-hydrogen cinchomerionate*, $C^7H^4NaNO^4$, forms almost colourless prismatic needles, which soon become opaque on exposure to the air, dissolve easily in water, but only sparingly in alcohol. *Sodium cinchomerionate*, $C^7H^3Na^2NO^4$, forms small, brilliant needles, which are easily soluble in water and in alcohol, and contain 2 mols. of water of crystallisation, which they lose at 110° . *Calcium cinchomerionate* has the composition $C^7H^2CaNO^4 + 3H_2O$ (Hoogewerff and van Dorp).

The fifth known modification of the acid $C^8H^4N(COOH)^2$ is obtained by oxidation of quinoline (from coal-tar) with potassium permanganate. It crystallises in short shining prisms slightly soluble in cold, more easily in hot water and alcohol, insoluble in ether and in benzene; they blacken when heated, and melt at 222° – 225° , which is nearly the melting point of nicotinic acid (p. 1392); a circumstance which, together with the previous blackening, renders it probable that the dicarboxylic acid is converted by heating into a monocarboxylic acid. The *barium salt* of this pyridine-dicarboxylic acid, $C^8H^3NO^4Ba$, and the *silver salt*, $C^8H^3NO^4Ag$, are gelatinous precipitates which become crystalline when heated for some time in a water-bath. The *calcium salt* when heated gives off an odour of Dippel's oil (Hoogewerff and van Dorp, *Ber.* xii. 747; xiii. 61).

Cinchonine-quinoline, oxidised by potassium permanganate, also yields a pyridine-dicarboxylic acid, which appears to be identical with that just described. It is sparingly soluble in cold water, and the aqueous solution gives with ferrous sulphate a reddish-yellow coloration, with copper acetate a pale blue precipitate, and with silver nitrate a precipitate soluble in hot water (W. Kænigs, *Ber.* xii. 983).

Pyridine-tricarboxylic Acid, $C^8H^3NO^6 = C^8H^2N(COOH)^3$. An acid of this composition is obtained by oxidation of quinine, quinidine, and cinchonidine. When quinine sulphate is oxidised at boiling heat by potassium permanganate in alkaline solution (8.5–9.5 g. $KMnO^4$ to 16 g. dry quinine sulphate), from 22 to 26 per cent. of its carbon is obtained as oxalic acid, and from 41.2 to 43.4 per cent. of its nitrogen as ammonia; and the resulting liquid contains, besides other nitrogenous bodies, a quantity of the acid $C^8H^3NO^6$, amounting to about 15 per cent. of the quinine sulphate. This acid retains $1\frac{1}{2}$ mol. crystallisation-water at 100° , which it gives off at 120° . It blackens at 190° , and melts at 244° . It is sparingly soluble in cold water, easily in hot water and alcohol, almost insoluble in ether and in benzene. Heated with lime in excess, it gives off the odour of the bases from Dippel's oil. Its *barium salt*, $(C^8H^2NO^6)^2Ba$, is nearly insoluble in water, and is obtained on adding barium acetate to a cold aqueous solution of the acid, as an amorphous precipitate, which is converted into a mass of small needles when heated in the liquid. The *calcium salt*,

Pyridine-dicarboxylic Acids.

α	β	γ
<i>Crystalline Forms :</i>		
Hair-like needles, changing in the mother-liquor to plates resembling naphthalene, and then to short prisms.	Granular microscopic octohedrons.	Spear-shaped crystals.
<i>Solubility :</i>		
Moderately soluble in water. More soluble in alcohol. Easily soluble in ether.	Soluble with difficulty in water. More soluble in alcohol. Sparingly soluble in ether.	Moderately soluble in water. Easily soluble in alcohol and ether.
Decomposing point, 237.5°.	244°-245°.	241°-245°.
<i>Salts :</i>		
<i>Ammonium Salt.</i> —Small soluble plates.	Moderately soluble needles.	Soluble needles.
<i>Calcium Salt.</i> —Contains no water. Sparingly soluble. Small needles.	Contains 2H ² O. Microscopic needles. Sparingly soluble.	Contains 2H ² O. Small plates. Sparingly soluble.
<i>Barium Salts.</i> —Neutral salt. Contains H ² O, and resembles the calcium salt.	Slightly soluble.	Soluble.
<i>Acid Salt.</i> —Very sparingly soluble.	—	—
<i>Potassium Salts.</i> —Neutral salt. Very soluble. Contains 1½H ² O.	Soluble.	Soluble.
<i>Acid Salt.</i> —Globular masses, consisting of tufts of needles radiating from a common centre.	—	—
<i>Lead Salt.</i> —Short prisms. Sparingly soluble.	White crystalline precipitate.	White crystalline precipitate.
<i>Copper Salts.</i> —(1). Light blue needles. (2). Dark blue prisms.	Light blue precipitate.	Whitish-blue precipitate.
<i>Silver Salts.</i> —(1). Neutral Salt:—Bulky, white, insoluble, gelatinous precipitate. (2). Acid Salt.—Ditto.	Very sparingly soluble crystalline precipitate.	Very sparingly soluble crystalline precipitate.
With <i>Ferric Chloride.</i> —No change of colour; a precipitate, even after addition of ammonia.	White flocculent precipitate, turning like ferric hydrate on addition of ammonia.	White flocculent precipitate, changed to ferric hydrate by ammonia.
<i>Copper Sulphate.</i> —No precipitate.	Whitish-blue precipitate.	Whitish-blue precipitate.
<i>Methyl Ether.</i> —Thick isolated crystals.	Deliquescent needles.	—
<i>Chloride.</i> —Crystalline mass. Melting point, 60.5°-61°. Boiling point, 284°.	Crystalline mass. Melting point, 49°. Boiling point, 269°-270°.	Crystalline mass. Melting point, 88°-89°. Boiling point, 265°.

($C^6H^2NO^6$) $\cdot Ca^2$, is sparingly soluble in water, and crystallises in concentric groups of small needles. The *normal silver salt*, $C^6H^2NO^6Ag^2$, precipitated from a solution of the acid neutralised with ammonia, appears to be amorphous. An *acid silver salt*, $C^6H^2NO^6Ag^2$, is thrown down from the aqueous solution of the acid as an amorphous precipitate, which afterwards becomes crystalline. The *normal potassium salt*, $C^6H^2NO^6K^2$, crystallises in white lustrous laminæ. The solution of the acid gives with *cupric acetate* a light blue amorphous precipitate; with *basic and normal lead acetate* white precipitates (Hoogewerff a. van Dorp, *Ber.* xii. 158).

Berberonic acid, obtained by oxidising berberine with nitric acid, has also the composition of pyridine-tricarboxylic acid. To prepare it, berberine is heated with eight to ten times its weight of nitric acid, and the resulting solution is concentrated, a crystalline mass then separating out on cooling. The acid is further purified by crystallisation from hot water and conversion into the calcium salt, which separates from the hot aqueous solution as a crystalline precipitate. The filtrate from the calcium salt has a yellow colour, and contains the salt of an acid which forms an insoluble silver salt, and may be separated therefrom in woolly needles; it has not been further investigated, as it occurs in very small quantities only (Weidel, *Ber.* xii. 410).

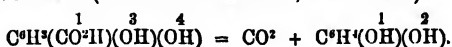
Berberonic acid, obtained by decomposing the calcium salt with an acid and crystallisation from hot water, forms groups of shining, transparent, prismatic crystals, which become opaque on exposure to the air. It is sparingly soluble in cold, easily in hot water; alcohol dissolves it but sparingly, and it is insoluble in ether, benzene, and chloroform. It has an acid taste, decomposes carbonates, and is decomposed by heat. When crystallised from dilute aqueous solutions, it forms triclinic prisms, which have the composition $C^6H^2NO^6 + 2H^2O$, and on exposure to air lose 1 mol. of water and become opaque. The aqueous solution of berberonic acid, like those of oxycinchomeronic acid (p. 484) and pyridine-dicarboxylic acid, gives, with ferrous sulphate, in the absence of a stronger acid, a deep red coloration.

Calcium berberonate, ($C^6H^2NO^6$) $\cdot Ca^2 + 4H^2O$, prepared by treating the ammoniacal solution of the acid with calcium chloride, separates out in white shining needles, which after one crystallisation are insoluble in water. The *cadmium salt*, ($C^6H^2NO^6$) $\cdot Cd^2 + 2H^2O$, crystallises in shining branching needles, and is sparingly soluble in water. The *silver salt*, $C^6H^2NO^6Ag^2$, is obtained as a white crystalline precipitate. The calcium salt, distilled with lime, yields pyridine, together with other products: $C^6H^2NO^6 = 3CO^2 + C^6H^2N$. When the acid is fused with potash, ammonia and hydrogen are evolved, and potassium cyanide and acetate are formed.

Berberonic acid closely approximates in percentage composition to the so-called oxycinchomeronic acid, which, as already observed, it also resembles in its reaction with ferrous salts. The following table gives a comparative view of the observed properties of these two acids:

	Oxycinchomeronic	Berberonic
Crystalline form.	Orthorhombic.	Triclinic.
Water of crystallisation	10.84 per cent.; does not effloresce.	14.57 per cent.; effloresces quickly.
Calcium salt	Cauliflower-like crusts; 25.3 per cent. water.	Fine, flexible needles; 21.1 per cent. water.
Cadmium salt	White crystalline powder; 12.2 per cent. water. Precipitated by copper acetate in the cold.	Needles having a satiny lustre; 8.73 per cent. water. Precipitated only when hot, the precipitate redissolving on cooling.

PYROCATECHOL or **CATECHOL**, $C^6H^4(OH)^2$ [1 : 2]. *Pyrocatechin* (see *Nomenclature*, p. 1420).—This modification of dihydroxybenzene is formed: *a.* By the action of melting potash on orthochlorophenol (vii. 906). *B.* By the dry distillation of protocatechuic acid (Tiemann a. Haarmann, *Ber.* vii. 608):



The resolution of protocatechuic acid into carbon dioxide and catechol takes place also by putrefaction in contact with pancreas. An infusion of the leaves of *Ampelopsis hederacea* left in contact with pancreas also yields catechol. Moreover, when protocatechuic acid is given to animals in their food, part of it is resolved in the organism into CO^2 and catechol, which passes into the urine in the form of a sulphonic acid.

The urine of a rabbit fed on milk diet was free from catechol, but after addition of an infusion of *Ampelopsis hederacea*, catechol was found in the urine.

The following method of preparing catechol from guaiacol (methyl-catechol) is given by Baeyer (*Ber.* viii. 155), the material used being the portion of Rhenish beech-tar creasote which distils at 200°–205°. The guaiacol, under the influence of dry hydrogen iodide at 195°–200°, splits up completely into catechol and methyl iodide. The operation is stopped as soon as red streaks show themselves on the sides of the glass, and the evolution of methyl iodide ceases. The residue is then fractionated, and the portion which distils between 220° and 250° is crystallised. By this process 1 kg. beech-tar creasote yielded 46 g. catechol. The smallness of the product is perhaps due to the presence of liquid phenols in the impure guaiacol employed.

The purification of catechol is best effected by recrystallisation from anhydrous benzene, in which it is much more soluble than resorcinol; the solution on cooling deposits it in perfectly colourless highly lustrous laminæ melting at 104° (Fittig & Mager, *Ber.* viii. 365).

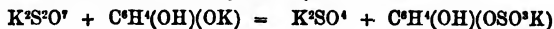
Nitrocatechol, $C^6H^3(NO^2)(OH)^2$, is formed by the action of nitrous acid in aqueous solution on catechol. 4 g. catechol and 20 g. commercial potassium nitrite are dissolved in 120 g. water; dilute sulphuric acid is added as long as effervescence is thereby produced; the dark brown-red liquid is shaken as rapidly as possible with an equal volume of ether; and the residue left after the expulsion of the ether is purified by recrystallisation from benzene. Nitrocatechol thus obtained forms very small woolly needles easily soluble in water, alcohol, and ether, sparingly in benzene, melting at 157° (uncorr.), and decomposing at a higher temperature. In potash-ley it dissolves with fine purple colour, and the reaction is so delicate that nitrocatechol might be used as an indicator in titration. *Normal barium-nitrocatechol*, $C^6H^3(NO^2O^2Ba, 3H^2O$, forms dark-red metallicallly lustrous laminæ, very sparingly soluble in water even at the boiling heat. At 130° they give off their water of crystallisation and assume a dark green colour, but do not lose their metallic lustre. The *acid barium salt* is much more soluble, and has not been obtained in the crystalline form.

Nitric acid completely decomposes nitrocatechol, with violent evolution of gas. By tin and hydrochloric acid it is converted into amidocatechol, the hydrochloride of which crystallises from dilute hydrochloric acid in long needles; the free base separated from this salt by alkalis oxidises immediately on exposure to the air, and dissolves with dark violet colour. By the action of nitrous acid on catechol in ethereal solution, another nitro-derivative is formed, which dissolves but sparingly in water, volatilises with water-vapour, and separates in yellow drops which soon solidify.

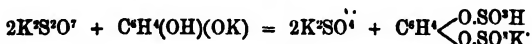
Dibromodimethylcatechol, or *Dibromoveratrol*, $C^6H^3Br^2O^2$, is contained in the red resin which is formed by the action of bromine on veratric acid. When crystallised from dilute alcohol, it forms hard shining prisms which melt at 83°–84°, are insoluble in water, but dissolve readily in alcohol and ether.

Nitrodimethyl-catechols. See VERATROLS (NITRO-).

Catecholsulphonic acids.—Two of these acids, $C^6H^4(OH).O.SO^3H$ and $C^6H^4(O.SO^3H)^2$, are obtained as potassium salts by the action of potassium pyrosulphate on a solution of catechol in potash-ley:



and

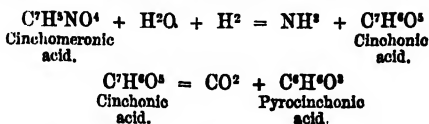


To prepare these salts, 20 pts. of catechol are added to a solution of 20 pts. potassium hydroxide in 25 pts. water, and the cooled mixture is agitated for several hours with 45 pts. potassium pyrosulphate, then heated on a water-bath, and exhausted with not more than an equal volume of absolute alcohol, whereby the catecholdisulphonate is separated, while the monosulphonate remains in the mother-liquor. *Potassium catecholdisulphonate* is a crystalline powder, insoluble in absolute alcohol; its aqueous solution gives no colour-reaction with ferric chloride. The *monosulphate* crystallises on evaporation of its ethereal solution in shining laminæ easily soluble in water; its aqueous solution gives a violet coloration with ferric chloride (E. Baumann, *Ber.* xi. 1907).

PYROCHLORE. On a variety of pyrochlore from the limestones of the Kaiserstuhl-range, see KOPPEL (p. 1158).

PYROCHROÏTE, MnH^2O^2 . This mineral occurs, together with manganosite, in a porous limestone rock in the Mossgrube, Wermland, Sweden (Sjögren, *Jahrb. f. Min.* 1877, 538).

PYROCINCHONIC ACID, $C^{10}H^{10}O$. Weidel obtained this acid by the dry distillation of cinchonic acid (p. 485), and assigned to it the formula $C^{10}H^{10}O^4$. Subsequent experiments have, however, shown that the formulæ originally assigned to this acid, and to cinchonic and cinchomeronic acids, were incorrect, and that the true reactions between these acids are represented by the formulæ:



Pyrocinchonic acid crystallises in pearly rhombic plates, has a sweet taste and alkaline reaction, melts at 90° , boils at 214° (uncorr.) Its vapour-density by experiment is 4.16; by calculation for $C^8H^8O^2$, 4.35 (Weidel a. von Schmidt, *Ber.* xii. 1146).

PYROCITRIC ACID. See CITRIC ACID (pp. 511-518).

PYROGALLOL, $\text{C}_6\text{H}_3(\text{OH})_3$. *Pyrogallollic acid*. *Oxidation*.—When a solution of pyrogallol, mixed with sodium phosphate, is exposed to the air, carbon dioxide is evolved, and pyrogalloquinone, $\text{C}_6\text{H}_2\text{O}_6$, is formed, identical with that which Wichelhaus obtained by dissolving quinone in pyrogallol (vii. 1030). This compound may be separated by ether from two other bodies formed in the reaction, one of these (an acid) being taken up by ether only after the mixture has been acidulated, and the other being nearly insoluble therein. An action similar to that of the phosphate, but less energetic, is exerted by the alkali-salts of weak acids, such as acetic and boric acids. Sodium thiosulphate effects rapid oxidation, but only as a carrier of oxygen; ammonium sulphate, magnesium sulphate, and potassium iodide exert but a feeble action; the chlorides, nitrates, and sulphates of potassium and sodium none at all.

On the oxidation of pyrogallol by *ozone*, see vii. 1029, 1030.

Pyrogallol absorbs *nitrogen dioxide* and *cyanogen*, forming with the latter the compound $C^H^O^3.CN$, which decomposes gradually at ordinary temperatures, and more quickly at 100° , yielding a brown-red resinous residue, soluble in alcohol, and sublimable in needles probably consisting of pyrogallol.

Reaction with Alkalis and Alkaloids.—Water containing an alkaline carbonate or an acid carbonate of calcium or magnesium gives in a few minutes, after addition of pyrogallol, a copious black precipitate. Alkaloids form with pyrogallol more or less brown solutions which give a black precipitate with *mercuric chloride*. A solution of mercuric chloride and pyrogallol in alcohol may therefore be used as a test for distinguishing plant-bases from glucosides, bitter principles, &c., more or less resembling them. A solution of 0.5 grm. pyrogallol in 5 c.c. water and 5 c.c. alcohol, mixed with 0.0001 grm. *ferrie chloride*, colours crystals of organic bases blue, whereas glucosides are not altered by it. Similar results are obtained with a solution of pyrogallol and *cupric chloride* (Schlagdenhauffen, *Pharm. J. Trans.* [3], iv. 772).

On the reaction of Pyrogallol with *Iron salts*, see vii. 1029.

Reaction with Picric Acid and Potassium Cyanide.—On mixing very strong solutions of pyrogallol (5 grms.), picric acid (10 g.), and potassium cyanide (20 g.), a salt is formed very much like potassium isopurpurate, but apparently less disposed to crystallise. Acids throw down from this solution a purple precipitate; copper, calcium, and barium salts a purple red or leather-coloured precipitate. Stannic chloride produces a light crimson coloration. Ferrous sulphate forms with the solution of this salt a red liquid which, on exposure to the air, deposits a dirty-green precipitate. The solution of the salt decomposes slowly on standing, more quickly at the boiling heat, with separation of a purple precipitate nearly insoluble in water and in cold alcohol. Potassium ferricyanide, added to the solution of the salt, throws down green flocks which dissolve, with apparent decomposition, when washed with water, and dissolve with green colour in alcohol (J. Walz, *Amer. Chem.* 1874, iv. 214).

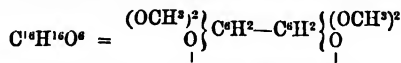
Reaction with Nitrogen Dioxide.—According to Russell a. Lapraik (*Chem. Soc. J.* xxxii. 35), a solution of potassium-pyrogallol absorbs 58 to 59 vol. p. c. of nitrogen dioxide when left in contact with it for twelve to fifteen hours. A solution of the same salt, saturated with oxygen, absorbs 76 per cent. Solution of potassium hydroxide absorbs 75 to 77 per cent. of the dioxide. Pyrogallol produces no alteration either in dioxide or monoxide of nitrogen. Potassium-pyrogallol does not act on the monoxide.

On the action of Bromine in presence of Water on Tribromopyrogallol, see vii. 1031; also XANTHOGALLOL in this volume.

Pyrogallic Ethers.

Dimethyl Pyrogallate, $C^6H^3(OH)(OCH^3)^2$ (A. W. Hofmann, *Ber.* xi. 333). This ether occurs in beech-tar oil, and is the constituent from which cedrret or cœrulignone (i. 818; vii. 376; viii. 548) is produced. To isolate it, the portion of beech-tar oil which boils at 250° – 270° was treated with benzoyl chloride, and the crystalline product (m. p. 107° – 110°) thereby obtained was decomposed by an alkali. The oil thus obtained, boiling between 250° and 265° , yielded on cooling splendid white prisms of dimethyl pyrogallate, melting at 51° – 52° , boiling constantly at 253° , and resolved by heating with hydrochloric acid into methyl chloride and pyrogallol. The ether may be prepared by heating for four or five hours at 150° – 160° , a mixture of 1 mol. pyrogallol, 2 mols. potassium hydroxide, and 2 mols. methyl iodide dissolved in methyl alcohol.

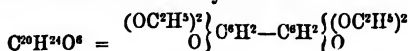
The conversion of the dimethyl pyrogallate into cedrret may be effected by various oxidising agents, viz. chlorine, bromine, iodine, nitric acid, ferric chloride, potassium ferricyanide, but not by atmospheric oxygen or ozone, and it succeeds best with potassium dichromate in glacial acetic acid, or by adding hydrochloric acid to a hot solution of the ether in soda-ley mixed with potassium dichromate. It appears most probable that an intermediate product, not yet isolated, is formed in the first instance, and then converted by further oxidation into cedrret or cœrulignone,



Ethyl Pyrogallates and the Cedrret of the Ethyl Series (Benedikt, *Ber.* ix. 125; Hofmann, *Ber.* xi. 797). Benedikt finds that pyrogallol cannot be ethylised by means of ethyl iodide, even when an alcoholic solution of the two bodies is heated in a sealed tube at 120° . The mono- and di-ethylic ethers may, however, be prepared, both from pyrogallol and from tannin, by the method adopted by Gorup-Besanez for the preparation of guaiacol (ii. 653). For this purpose the requisite quantities of potassium hydroxide and potassium ethylsulphate are introduced into a champagne or soda-water bottle, and 20 grams of pyrogallol and about 300 c.c. of absolute alcohol are added. The bottle is then tightly closed, and heated for twenty-four hours in a water-bath. When the action is over, the product is supersaturated with sulphuric acid, and shaken with ether; the ether is then removed by distillation; the thick oil which remains is washed with water and distilled; and the distillate, which is a mixture of the solid mono- and the liquid di-ethylic ether, is separated into its two constituents by pipetting. Hofmann, by proceeding in a similar manner, using 1 mol. pyrogallol, 3 mols. potassium hydroxide, and 3 mols. potassium ethylsulphate, has obtained all the three ethylic ethers of pyrogallol. To separate them from the crude product, the alkaline liquid is saturated with hydrochloric acid, the alcohol then removed by distillation in the water-bath, and the dry strongly coloured residue well shaken with ether, which, on evaporation, leaves a dark brown oil having a strong odour of beech-tar. This oil may be freed from unaltered pyrogallol by washing with an equal volume of water, and then treated with soda-ley, whereupon the mono- and di-ethylic ethers dissolve, while the triethylic ether remains undissolved. If the mixture of the three ethers be treated with an insufficient quantity of soda-ley, only the monethylic ether passes into solution.

Monethyl Pyrogallate, $C^6H^3(OH)(OC^2H^5)$, forms crystals melting at 95° , very easily soluble in alcohol and ether, sparingly soluble in cold, more freely in hot water. It crystallises from alcohol in hard needles, from water in small slender needles; volatilises with vapour of water (Benedikt).

Diethyl Pyrogallate, $C^6H^3(OH)(OC^2H^5)^2$, was described by Benedikt as a liquid which did not solidify at -10° , volatilised with vapour of water, and resembled the monethylic ether in its relations to solvents. According to Hofmann, however, it separates from very dilute alcohol in crystals which melt at 79° . When dissolved in glacial acetic acid, and treated with potassium dichromate, it is converted into ethylcedrret, or rather the cedrret of the ethyl-series:



This compound is insoluble in water and in ether, soluble in alcohol, and crystallises in long thin crimson needles, which have a bluish-green shimmer like that of cantharides, become light red when dried or pulverised, and dissolve with cornflower-blue colour in strong sulphuric acid. *Hydroethylecdrret* or *Tetretoxy-dihydroxydiphenyl*,

$(\text{OH})(\text{OC}^2\text{H}^3)\text{C}^2\text{H}^2-\text{C}^2\text{H}^2(\text{OC}^2\text{H}^3)^2(\text{OH})$, formed by the action of sulphurous acid on ethyl-cedriret, melts with decomposition at 176° , is insoluble in water, easily soluble in ether, and is converted by oxidising agents into cedriret.

Triethyl Pyrogallate, $\text{C}^2\text{H}^2(\text{OC}^2\text{H}^3)^3$, crystallises in long needles melting at 39° , resembles the two preceding in most of its physical characters, but is not dissolved by soda-ley (Hofmann).

Ethylene Pyrogallate, $\text{C}^2\text{H}^2\text{O}^2=\text{C}^2\text{H}^2(\text{OH})\langle\bigcirc\rangle\text{C}^2\text{H}^2$ (Magatti, *Ber.* xii. 1860),

is prepared by heating 2 mols. pyrogallol, 3 mols. ethylene bromide, and 6 mols. potash with ethyl alcohol at 100° for fifteen to twenty hours; and may be separated from the product by acidifying with hydrochloric acid and extracting with ether. the ethereal extract yielding it on rectification as a colourless, heavy, strongly refractive liquid having a burning taste, and the odour of beech-wood tar; it boils at 267° . It resembles the phenols in its properties, forming crystalline compounds with alkalis, benzoic chloride, and bromine. The *benzoyl compound*, $\text{C}^2\text{H}^2\text{O}^2(\text{OC}^2\text{H}^3\text{O})$, is a white crystalline substance, easily soluble in boiling alcohol and ether, melting at 109° . The bromo-compound crystallises from glacial acetic acid in transparent tables melting at 67° .

Monethylene pyrogallate is easily oxidised by ferric chloride and potassium dichromate; but the oxidation-product is apparently not uniform in composition. It is not dissolved but blackened by sulphuric acid, and therefore differs from the class of compounds to which cedriret belongs.

Simultaneously with the ethylene pyrogallate there is formed a compound which is insoluble in alkalis, soluble in alcohol and ether, separates from the former in ill-defined crystals melting at 83° , and apparently having the composition $\text{C}^2\text{H}^2\text{O}^2\text{Br}$.

Methyl-pyrogallol, $\text{C}^2\text{H}^2\text{O}^2=\text{C}^2\text{H}^2(\text{CH}^3)(\text{OH})^2$. The dimethylic ether of this phenol is obtained, together with those of pyrogallol and propyl-pyrogallol, by treating the crude mixture of pyrogallic ether extracted from beech-wood tar (p. 1710) with benzoic chloride. The resulting benzoyl-compounds are separated by fractional crystallisation; that of methyl-pyrogallol melts at $118^\circ-119^\circ$, and is resolved by potash into benzoic acid and *dimethylic methylpyrogallate*, $\text{C}^2\text{H}^2(\text{CH}^3)(\text{OH})(\text{OCH}^3)^2$, which melts at 36° and boils at 265° . This ether, heated at $150^\circ-160^\circ$ with strong hydrochloric acid, yields methyl chloride and methyl-pyrogallol, which is soluble in water, melts at 129° , and volatilises unchanged. It bears a strong resemblance to pyrogallol, its alkaline solution turning brown on exposure to the air (Hofmann, *Ber.* xii. 1371).

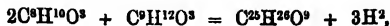
Propyl-pyrogallol, $\text{C}^2\text{H}^2\text{O}^2=\text{C}^2\text{H}^2(\text{C}^2\text{H}^5)(\text{OH})^2$. The dimethylic ether of this compound, $\text{C}^2\text{H}^2\text{O}^2=\text{C}^2\text{H}^2(\text{C}^2\text{H}^5)(\text{OH})(\text{OCH}^3)^2$, constitutes the portion of beech-tar oil which boils at 285° . Treated with acetic anhydride, it yields an acetyl-derivative, $\text{C}^2\text{H}^2(\text{C}^2\text{H}^5\text{O})\text{O}^2$, which melts at 87° , is insoluble in water, crystallises from alcohol in white prisms, forms with bromine a dibromo-derivative, $\text{C}^2\text{H}^2\text{Br}^2(\text{C}^2\text{H}^5\text{O})\text{O}^2$, melting at $101.5^\circ-102.5^\circ$, and with benzoyl chloride a benzoyl-derivative melting at 91° .

By heating the oil or its acetyl-derivative with strong hydrochloric acid at 130° in a sealed tube, methyl chloride is produced, together with propyl-pyrogallol, which dissolves easily in water, alcohol, and ether, and crystallises in prisms melting at $79^\circ-80^\circ$ (Hofmann, *Ber.* xi. 329).

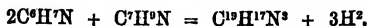
Colouring Matters from Pyrogallic Ethers. The formation of cedriret from dimethylic pyrogallate has already been mentioned, and further experiments have shown that pittacal, the blue colouring matter which Reichenbach obtained from the high-boiling portions of wood-tar, belongs to the same class of bodies. The process by which Reichenbach prepared this body is not known, but Grätzsl, in Hanover, by subjecting the higher-boiling portions of wood-tar to a peculiar process of oxidation (not yet published), has obtained a brown earthy substance which gives with baryta the blue reaction described by Reichenbach. This brown substance has been examined by Liebermann (*Ber.* ix. 334), who finds that the colouring matter, which is present in small quantity only, may be isolated by digesting the brown substance with hot acetic acid, mixing the filtered solution with excess of neutral lead acetate, treating the resulting precipitate with hydrogen sulphide, and exhausting the washed lead sulphide with warm alcohol, which dissolves the colouring matter, and leaves it on evaporation as an orange-red crystalline powder.

The colouring matter is soluble in alcohol and acetic acid, forming brown solutions. Alkalis dissolve it with purple, ammonia with blue colour, forming solutions from which carbon dioxide throws down blue salts soluble in pure water. In the alkaline solutions calcium, magnesium, barium, and tin salts produce blue precipitates, often

agents convert dimethylic pyrogallate into cedret. The reaction may be thus represented :



and may be compared with that by which rosaniline is produced from aniline and toluidine :

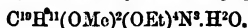


In the former case the oxygen necessary to remove hydrogen is derived from the atmosphere, as may be proved by attempting to conduct the reaction out of contact with air.

Eupittonic acid appears to be bibasic. Its alkali-salts are blue with green reflex. The ammonium salt is decomposed when its solution is boiled, and after a time crystals of pittacal are deposited. In virtue of the intensely blue colour of the alkaline compounds of pittacal, paper steeped in a solution of it and dried, furnishes an exceedingly sensitive test for free alkalis, but its utility for this purpose is considerably lessened by the fact that hydrochloric acid also colours it blue.

When boiled with acetic anhydride, eupittonic acid yields a yellow diacetyl derivative, which strangely enough is insoluble in alkalis, although its molecule ought still to contain four hydroxyl groups.

A homologue of eupittonic acid, $\text{C}^{20}\text{H}^{34}\text{O}^9$ (which has not been analysed), was prepared by heating *diethylic pyrogallate* and *dimethylic methylpyrogallate* with soda. It differs from its prototype in being soluble in ether and less easily crystallisable, and in the inferior stability of its ammonium compound. It also forms a triamine when heated with ammonia, probably a *dimethoxyl-tetretoxyl pararosaniline* :



PYROGALLOQUINONE, $\text{C}^{12}\text{H}^{10}\text{O}^2 = \text{C}^6\text{H}^4 \begin{smallmatrix} < \text{O.O.C}^6\text{H}^3(\text{OH})^2 \\ \text{O.O.C}^6\text{H}^3(\text{OH})^2 \end{smallmatrix}$. This compound, which Wichelhaus obtained, together with quinol, by dissolving quinone in pyrogallol (vii. 1030), according to the equation $2\text{C}^6\text{H}^4\text{O}^2 + 2\text{C}^6\text{H}^6\text{O}^2 = \text{C}^6\text{H}^6\text{O}^2 + \text{C}^{12}\text{H}^{10}\text{O}^2$, is also produced by oxidation of pyrogallol in the air in presence of sodium phosphate (p. 1709), and may be separated by agitation with ether from two other bodies formed at the same time, one of which (an acid) dissolves in ether only after acidulation of the mixture, while the other is nearly insoluble in ether. To prepare the quinone in considerable quantity, 10 grams of pyrogallol are mixed with 25 g. sodium phosphate and 250 c.c. water, and the whole is heated to 50° , and agitated for half an hour in an apparatus constructed for the purpose.

Pyrogalloquinone is sparingly soluble in water, somewhat more soluble in alcohol, still more in ether, chloroform, and sodium phosphate. It reduces Fehling's solution and silver nitrate. Its aqueous solution gives a blue-violet precipitate with ferrous salts, red-brown precipitates with copper and lead salts, and produces a dark colour with ferric chloride. The blue colour which Wichelhaus observed on treating pyrogalloquinone with alkalis is produced only in presence of free oxygen (O. Loew, *J. pr. Chem.* [2], xv. 322).

PYROGENTISIC ACID, $\text{C}^6\text{H}^6\text{O}^2$. This substance, obtained by the action of heat on gentisic acid, the colouring matter of gentian root (p. 860), and at first supposed to be isomeric with quinol (hydroquinone), has since been shown to be identical therewith, the error having arisen from incorrect determination of the melting point of quinol, which is now known to melt at 169° . In like manner, gentisic acid has been shown to be identical with hydroxysalicylic acid (m. p. 196° – 197°) (Hlasiwetz a. Habermann, *Liebig's Annalen*, clxxx. 343).

PYROLUSITE, MnO^2 . Analyses of this mineral have recently been published by Phipson (*Chem. News*, xxxiii. 243), Muir (*ibid.* xxxv. 6), and by Wright a. Luff (*Chem. Soc. J.* xxxv. 518).

PYROMARIC ACID. See PIMARIC ACID (p. 1626).

PYROMECAZONIC ACID. See the next article.

PYROMECONIC ACID, $\text{C}^8\text{H}^4\text{O}^3$ (Ost, *J. pr. Chem.* [2], xix. 34 and 177. Ihlé, *Liebig's Annalen*, clxxxviii. 31). This acid, isomeric with pyromucic acid, is formed from meconic acid, $\text{C}^8\text{H}^4\text{O}^7$, by elimination of 2 mols. CO^2 . It crystallises in large brilliant prisms, easily soluble in water and in alcohol, less soluble in ether and in chloroform; volatilises completely at 100° ; boils at 225° (Ost); melts at 121.5° , and boils at 227° – 228° (Ihlé). In contact with excess of alkali it readily oxidises, even without warming, producing formic acid (Ost). On boiling it with baryta-water, the liquid turns red and brown, and deposits a precipitate of barium carbonate, and

the aqueous distillate yields drops of an oil which reduces silver salts (perhaps an aldehyde). The residue of the distillation contains barium formate (Ihlée).

Pyromeconic acid unites with hydrochloric and sulphuric acid. When gaseous *hydrochloric acid* is passed over it, only a very small quantity is taken up, but on mixing the ethereal solutions of pyromucic acid and phosphorous chloride, white needle-shaped crystals quickly separate, having the composition $C^5H^3O^2.OH.HCl$. This compound is resolved into its constituents by alcohol or water, and slowly by moist air. The corresponding *sulphate*, $(C^5H^3O^2.OH)^2.H^2SO^4$, separates in prismatic crystals from a mixture of 1 mol. pyromeconic acid in ethereal solution and less than 1 mol. sulphuric acid; if the two acids are mixed in equal numbers of molecules, needle-shaped crystals separate, having the compound $C^5H^3O^2.OH.H^2SO^4$.

Pyromeconates. Besides the normal salts of the general formula $C^5H^3MO^3$, pyromeconic acid forms acid salts, $C^5H^3MO^3.C^5H^4O^3$, which easily part with a molecule of pyromeconic acid; both series of salts crystallise well and have an acid reaction. The *normal potassium salt*, $C^5H^3KO^3$, is prepared by mixing excess of potash with a concentrated solution of the acid; if a somewhat dilute solution be used, the acid is oxidised, with production of formic acid (Ost). Ihlée prepares the salt by mixing a hot alcoholic solution of the acid with alcoholic potash, the salt then separating on cooling as a crystalline pulp. The normal sodium salt has not been obtained; the *acid sodium salt*, $C^5H^3NaO^3.C^5H^4O^3$, is formed on mixing the alcoholic solution of the acid and base. An *ammonium salt* of uncertain composition, and easily undergoing decomposition, with reproduction of the acid, is formed on mixing alcoholic solutions of the acid and ammonia; if aqueous solutions are used and much ammonia is added, pyromeconic acid alone crystallises out (Ost). The *acid barium and calcium salts*, $(C^{10}H^7O^4)^2M = (C^5H^3O^3)^2M.2C^5H^4O^3$, are obtained by boiling the respective carbonates with a solution of the acid till the liquid becomes neutral; on longer boiling, decomposition takes place. The *copper salt*, $(C^5H^3O^3)^2Cu$, crystallises in green silky needles (Ihlée).

No ethereal salts of pyromeconic acid have been obtained. *Acetylpyromeconic acid*, $C^5H^3(C^2H^3O)O^3$, is easily prepared by heating the acid with acetyl chloride, and crystallising the product from absolute alcohol; it forms colourless prisms melting at 91° , easily soluble in alcohol, water, and chloroform.

Nitropyromeconic Acid, $C^5H^3(NO^2)O^3$, is formed, with violent reaction, on adding 1 to $1\frac{1}{2}$ pts. strong nitric acid to 2 pts. pyromeconic acid dissolved in 6 pts. acetic acid, and crystallises from alcohol in small well-defined yellow prisms, very slightly soluble in cold water, and decomposed with explosion by boiling water; insoluble in ether, benzene, chloroform, and carbon sulphide; dissolves most readily in absolute alcohol, acetone, or hot acetic acid.

The acid is monobasic. Its *sodium salt*, $C^5H^2(NO^2)NaO^3$, obtained by heating the nitro-acid with aqueous sodium carbonate, crystallises on cooling in golden-yellow laminae slightly soluble in cold water. It is quickly decomposed by excess of sodium carbonate or hydrate, even at ordinary temperature. It explodes with great violence when heated, also when moistened with a drop of strong sulphuric acid. The *barium and calcium salts* are obtained by double decomposition as crystalline precipitates. The *silver salt*, obtained by gently warming the aqueous acid with silver nitrite, forms orange-yellow crystalline nodules, insoluble in cold water; its formation serves for the detection of very small quantities of the nitro-acid. It is decomposed by water slowly in the cold, more quickly when heated, with separation of metallic silver; it explodes when heated alone.

Amidopyromeconic Acid, $C^5H^3(NH^2)O^3$. The hydrochloride of this acid, obtained by reducing the nitro-acid with tin and hydrochloric acid, removing the tin from the resulting double salt with hydrogen sulphide and evaporating, forms large rhombic crystals having the composition $C^5H^3(NH^2)O^3.HCl + H^2O$; and these, when decomposed by ammonia in aqueous solution, yield the acid, which crystallises from hot water in long needles, easily decomposed by alkalis, but not by water.

Nitrosodipyromeconic Acid, $C^{10}H^7(NO)O^6$, is obtained by passing nitrous gas (from arsenious oxide and nitric acid) into an ethereal solution of pyromeconic acid. It is very unstable, giving off hydrocyanic acid on exposure to moist air. It separates from the liquid as a light yellow precipitate, but cannot be crystallised, as the liquids which dissolve it also decompose it. Excess of nitrous acid readily converts it into nitropyromeconic acid. On warming it with water, nitrous and hydrocyanic acids are evolved, together with carbonic anhydride and other gases, and a moderately stable crystalline compound separates, having the composition $C^5H^3NO^3.C^5H^4O^3$. This compound, heated with chloroform, is decomposed, pyromeconic acid going into solution, and oxypyromecazonic acid, $C^5H^3NO^4$, remaining.

This last acid in its general character resembles pyromeconic acid; it is easily soluble in hot water, soluble in cold water and in alcohol, insoluble in ether and chloroform; crystallises in needles with 1 mol. of crystalline water, occasionally also with 2 mols., and in short anhydrous prisms.

It is readily decomposed by excess of alkali, and by oxidising agents generally: not attacked by hydrochloric acid.

Acid Sodium Oxypyromecazonate, $C^5H^1NaNO^4, C^5H^2NO^4$, separates as a crystalline pulp on mixing the free acid and sodium carbonate in the proportions to form the normal salt, which appears to be uncrystallisable. The white salt precipitated on adding a small quantity of soda to the alcoholic solution becomes deep blue on addition of more soda, but dissolves without colour in water. The *acid potassium salt*, produced like the sodium salt, crystallises in large anhydrous prisms. The *normal calcium salt*, $(C^5H^1NO^4) \cdot Ca$, is formed on mixing either the normal or the acid sodium salt with calcium chloride, as an amorphous precipitate which becomes crystalline on cooling; it is very slightly soluble in water, and when treated with ammonia, in contact with the air, gradually turns blue. The *barium salt*, formed like the calcium salt, is less stable in contact with the air. The *acid thallium salt*, obtained by precipitating the acid sodium salt with thallous sulphate, crystallises in very thin colourless anhydrous needles sparingly soluble in water.

Oxypyromecazonic acid combines with acids as well as with bases. The *hydrochloride*, $C^5H^1NO^4 \cdot HCl$, obtained by dissolving the acid in gently warmed strong hydrochloric acid, crystallises on cooling in hard crusts (pyromeconic acid crystallises from fuming hydrochloric acid without alteration). The crystals, when left over quicklime, do not give off a trace of hydrochloric acid, but water immediately resolves them into their components. The *hydriodide* is obtained in like manner, and exhibits similar properties.

Pyromecazonic acid, $C^5H^1NO^3$, isomeric with amidopyromeconic acid, is produced by long-continued action, at a moderate temperature, of tin and hydrochloric acid upon the foregoing acid. After removing excess of tin, the liquid is evaporated, when a double compound of pyromecazonic acid and hydrochloric acid, $C^5H^2NO^3 \cdot HCl$, crystallises out. This compound is decomposed by water, the solution is evaporated to dryness to drive off hydrochloric acid, and pure pyromecazonic acid is obtained by recrystallising the residue from hot water. Pyromecazonic acid is but very slightly soluble in cold water, almost insoluble in alcohol, and insoluble in ether: it may be partially sublimed unchanged. Its salts are unstable, being easily decomposed by the oxygen of the air, with production of blue and violet-coloured bodies. It forms double compounds with acids, and in its general behaviour resembles oxypyromecazonic acid (Ost).

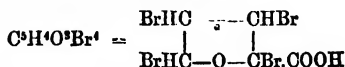
PYROMELLITIC ACID, $C^{10}H^6O^8 = C^5H^2(CO^2H)^4$. The methylic ether of this acid crystallises in large plates; melts at 138° ; distils without decomposition; and is but sparingly soluble in alcohol, even at the boiling heat (Baeyer, *Liebig's Annalen*, clxvi. 325).

On the compounds produced by the action of Pyromellitic acid on α -Naphthol, see vii. 840.

PYROMUCIC ACID, $C^5H^4O^3$. This acid is best obtained by the action of alcoholic potash on furfural. This aldehyde, in quantity not exceeding 25 grams, is mixed with an equal volume of concentrated alcoholic potash, whereupon the mixture becomes very hot, and solidifies in a few minutes to laminae of potassium pyromucate. The furfuralcohol formed at the same time is removed, after cooling, by washing with ether, and the pyromucic acid is precipitated from the residue by hydrochloric acid. The quantity of pyromucic acid thus obtained amounts to 33 per cent. of the furfural, whereas the method of decomposition by silver oxide yields only 14 per cent. Dry distillation of mucic acid yields but a very small quantity (Limpricht, *Liebig's Annalen*, clxv. 278).

On the Reactions and Isomerides of Pyromucic acid, see vii. 1032. On its Constitution, see p. 836 of this volume.

Bromine-compounds. *Dibromide of Pyromucic acid*, $C^5H^4O^3Br^2$, is formed on adding bromine to a solution of ethyl pyromucate in glacial acetic acid (R. Schiff a. G. Tassinari, *Ber.* xi. 842); and the *tetrabromide*,



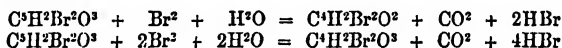
by exposing pyromucic acid to the action of dry bromine-vapour. This compound is a white crystalline substance easily soluble in alcohol and ether, sparingly in chloroform

and light petroleum, insoluble in cold water, decomposed by hot water with evolution of CO_2 and HBr . It melts with decomposition at $159^\circ\text{--}160^\circ$, giving off bromine and hydrogen bromide, and yielding an acid body in the form of a sublimate of needle-shaped crystals melting at 180° . By reducing agents it is converted into pyromucic acid; by oxidation with chromic acid, into dibromosuccinic acid (Tönnies, *Ber.* xi. 1085).

Tetrabromide of Ethyl Pyromucate, $\text{C}^4\text{H}^2\text{Br}^4\text{O}^3.\text{COOC}^2\text{H}^3$, is prepared by the action of dry bromine vapour on ethyl pyromucate for twelve hours at ordinary temperature, treating the product with a small quantity of bromine, and removing the excess of bromine with sulphurous acid. It dissolves in chloroform, and separates from the solution in colourless crystals which melt at $46^\circ\text{--}48^\circ$, and decompose at a higher temperature. Sodium-amalgam converts it into ethyl pyromucate (Tönnies).

Monobromopyromucic acid, $\text{C}^4\text{H}^3\text{BrO}^3$.—Two modifications of this acid are produced by the action of alcoholic potash on the dibromide of pyromucic acid, and are easily separated by taking advantage of the difference of their solubility in boiling water. The more soluble of the two crystallises in colourless needles which melt at 155° , sublime readily, and are converted into the less soluble modification by repeated boiling with water, and precipitation by hydrochloric acid. The less soluble acid, which may be purified by crystallisation from a large quantity of water or from dilute alcohol, forms beautiful micaceous scales melting at 180° (Schiff a. Tassinari, *Ber.* xi. 842; *Gazz. chim. ital.* 1878, 297).

Dibromopyromucic acid, $\text{C}^4\text{H}^2\text{Br}^2\text{O}^3$, formed in like manner from the tetrabromide, crystallises in colourless scales, which melt at $184^\circ\text{--}186^\circ$, and sublime without decomposition at a higher temperature (Tönnies, *loc. cit.*) When heated with bromine-water at ordinary temperatures it yields carbon dioxide and mucobromic aldehyde, $\text{C}^4\text{H}^2\text{BrO}^3$, which crystallises from ether in stellate groups of needles melting at 88° , easily soluble in water, ether, and chloroform. This aldehyde, gently heated with chromic acid solution, is converted into mucobromic acid, $\text{C}^4\text{H}^2\text{BrO}^3$, identical with that which is obtained by the direct action of bromine on pyromucic acid (vii. 828). The same oxidation may be effected by adding bromine-water to a boiling aqueous solution of dibromopyromucic acid till the colour of the bromine no longer disappears. It appears, therefore, that at ordinary temperatures only 1 mol. of bromine enters into the reaction with the result of forming an aldehyde, but that at higher temperatures 2 mols. of bromine enter into the reaction and produce the corresponding acid:



This last reaction is exactly analogous to that which takes place when pyromucic acid is treated with bromine-water at ordinary temperatures, whereby fumaric aldehyde is produced, and renders it probable that the difference in the behaviour of pyromucic and dibromopyromucic acid to bromine-water is due to the fact that, with the latter, the action stops at an intermediate stage, which, in the case of the non-brominated acid, is at once passed over. If this view be correct, mucobromic acid must be regarded as dibromofumaric aldehyde (Tönnies, *Ber.* xii. 1202).

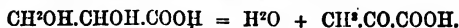
PYROPHOSPHATES. See PHOSPHATES (pp. 1601).

PYROPHYSALITE. See TOPAZ.

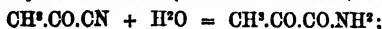
PYROPISSITE. This waxy substance, which occurs in lignite, was first described by Kennigott (iv. 769), and has lately been examined by H. Schwarz (*Dingl. pol. J.* ccxxxii. 465; *Chem. Soc. J.* xxxvi. 1022).

PYRORACEMIC or **PYRUVIC ACID**, $\text{C}^3\text{H}^4\text{O}^3 = \text{CH}^3.\text{CO}.\text{COOH}$, or

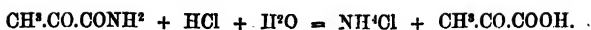
$\begin{array}{c} \text{CH}^2 \\ \diagdown \\ \text{O} \\ \diagup \\ \text{CH}.\text{COOH} \end{array}$. This acid is formed: 1. By boiling chloracrylic acid with silver oxide and water $\text{C}^3\text{H}^3\text{ClO}^2 + \text{AgHO} = \text{AgCl} + \text{C}^3\text{H}^4\text{O}^3$ (Beckurts a. Otto, *Ber.* x. 265). 2. By the action of strong sulphuric acid at $40^\circ\text{--}50^\circ$ on tartaric acid: $\text{C}^4\text{H}^4\text{O}^6 = \text{CO}_2 + \text{H}^2\text{O} + \text{C}^3\text{H}^4\text{O}^3$ (Bouchardat, *Compt. rend.* lxxxix. 99). 3. By the dry distillation of glyceric acid (Böttinger, *Liebig's Annalen*, cxvii. 92):



4. By mixing acetyl cyanide with an equivalent quantity of hydrochloric acid, sp. gr. 1.2, whereby it is converted into acetyl-formamide, and decomposing the latter with a slight excess of dilute hydrochloric acid (Claisen a. Shadwell, *Ber.* xi. 1563):



and

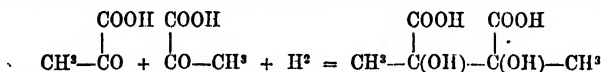


The first two of these modes of formation are consistent with either of the formulæ above given for the acid; the third is most readily explained by the first formula, and the fourth may be regarded as decisive in its favour.

Reactions. 1. *Decomposition by Heat.*—Pyroracemic acid, boiled for about eight hours in a reflux apparatus, gives off carbon dioxide, becomes continually thicker, and darker in colour, and on cooling solidifies to a resin from which boiling water extracts pyrotartaric, uvic, and a small quantity of acetic acid, the greater part, however, remaining undissolved. Hence it is probable that the pyrotartaric acid produced in the dry distillation of tartaric acid is a further product of decomposition of pyrорacemic acid, formed, in the first instance, according to the equation above given (Böttiger, *Ber.* ix. 670).

2. With *Phosphorus Pentachloride*.—When pyrорacemic acid is gradually run into 5 pts. of the pentachloride, hydrochloric acid, carbon dioxide, carbon monoxide, and a small quantity of acetyl chloride are produced; and on completing the dissolution of the pentachloride by warming, then distilling, pouring the portion which goes over at 130° into alcohol, and adding common salt, ethylic α-dichloropropionate, $\text{CH}^3\text{CCl}^2\text{COOC}^2\text{H}^5$ (m. p. 155°–160°), is obtained (Beckurts a. Otto, xi. 386; comp. Böttiger, vii. 1033).

3. With *Zinc*.—When an alcoholic solution of pyrорacemic acid is treated with zinc (and a small quantity of hydrochloric acid), or with zinc-dust, the following reaction takes place, resulting in the formation of dimethyl-tartaric acid, $\text{C}^2\text{H}^{10}\text{O}^6$, which is related to pyrорacemic acid in the same way as pinacone to acetone:



The zinc-salt of dimethylpyrotartaric acid separates during the reaction as a white precipitate quite insoluble in cold water, while zinc lactate and a salt apparently belonging to a modified pyrорacemic acid remain in solution (Böttiger, *Ber.* ix. 1064). These two reactions afford farther confirmation of the formula $\text{CH}^3\text{CO.CO}^2\text{H}$ for pyrорacemic acid.

4. With *Hydrocyanic acid*.—When pyrорacemic acid is left in contact for some time with highly concentrated hydrocyanic acid and a few drops of strong hydrochloric acid, an additive cyanogen-product is formed, which may be extracted from the liquid by ether. The residue left on evaporating the ether does not crystallise, and its aqueous solution forms no precipitate with silver nitrate, but gives off ammonia when boiled with alkalis. On heating it for two days with strong hydrochloric acid, carbon dioxide is given off, and ordinary lactic acid is formed. When large quantities of pyrорacemic acid, absolute hydrocyanic acid, and hydrochloric acid were heated together on the water-bath, a very violent reaction took place, and the product, when shaken with ether, yielded ordinary pyrotartaric acid, $\text{CH}^3\text{CH}(\text{CO}^2\text{H}).\text{CH}^2\text{COOH}$, together with mesaconic acid, $\text{CO}^2\text{H}.\text{CH}=\text{CH}.\text{CH}^2.\text{CO}^2\text{H}$ (Böttiger, *Ber.* ix. 1621).

5. With *Chromic acid mixture*.—Pyrорacemic acid, diluted with water and dropped into a cooled mixture of 10 grams potassium dichromate, 10 c.c. strong sulphuric acid, and 60 c.c. water, is completely resolved into acetic and carbonic acids, $\text{C}^2\text{H}^4\text{O}^3 + \text{O} = \text{C}^2\text{H}^4\text{O}^2 + \text{CO}^2$ (Böttiger, *Ber.* viii. 713).

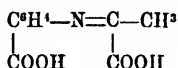
6. With *Barium Hydrate*.—Pyrорacemic acid, boiled with excess of barium hydrate, yields, according to Finck (iv. 770), uvitic acid, $\text{C}^2\text{H}^6\text{O}^4$, and uvitonic acid, $\text{C}^2\text{H}^{12}\text{O}^7$ (?), together with acetic, oxalic, and carbonic acids; with a quantity of barium hydrate, on the other hand, not sufficient to neutralise it, it yields uvic, pyrotartaric, acetic, carbonic acid, and two acids the nature of which has not been ascertained (Böttiger, *Ber.* vi. 787, 893). Further, when neutral barium pyrорacemate is heated for several days in a reflux apparatus, carbon dioxide escapes, the liquid after a while becomes acid; then again neutral, and a precipitate is formed, consisting of barium carbonate and oxalate. From the brownish filtrate hydrochloric acid throws down a mixture of uvic and uvitic acids, which may be separated by distillation with steam; and the same filtrate yields to ether, pyrotartaric, acetic, and a small quantity of uvic acid, still retaining a large amount of pyrotartaric and (probably) uvitonic acid. The products of decomposition of pyrotartaric acid in neutral solution consist, therefore, of the sum of those obtained in acid and in alkaline solution (Böttiger, viii. 957).

7. With *Ammonia*.—Gaseous ammonia acts very violently on pyrорacemic acid, eliminating carbon dioxide; and on treating the product with milk of lime, acetic acid is formed, together with modified pyrорacemic acid. Aqueous ammonia, heated with pyrорacemic acid, does not yield any product of decomposition. Alcoholic ammonia

yields—together with acetic acid and carbon dioxide—a precipitate consisting of the acid ammonium salt of an acid, $C^8H^8NO^4$, called by Böttinger uvitoninic acid (*Ber.* x. 362).

8. With *Aniline*.—On bringing this base in contact with pyroracemic acid, anilopyroracemic acid, $C^8H^8NO^2 = CH^3.C \begin{smallmatrix} \nearrow NC^6H^5 \\ \searrow COOH \end{smallmatrix}$, separates as a crystalline body which melts at 122° , and when dissolved in water is converted into an isomeric body which has not been obtained pure. The solution when heated yields pyroracemic acid, aniline, and acid bodies which are further acted on by the aniline, and ultimately a crystalline product is obtained, probably having the composition $C^{20}H^{20}N^2O^4$; it exhibits basic properties, combining with acids, and forming a platinochloride (Böttinger, *Ber.* x. 818).

9. With *Anthranilic acid* or [1 : 2] *Amidobenzoic acid*.—This acid acts violently on pyroracemic acid, forming a yellow powder which continuously gives off carbon dioxide at 135° , turns blue when exposed to light or suspended in water, and is perhaps constituted according to the formula:



(Böttinger, *Ber.* x. 1517; *Liebig's Annalen*, clxxxviii. 293).

10. With *Urea*.—Pyroracemic acid and urea, heated together at 100° , yield pyroracemic carbamides or ureides (p. 1720).

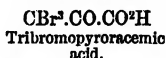
11. Silver pyroracemate, decomposed by *hydrogen sulphide*, yields thiolactic acid, $C^3H^4SO^2$ (Böttinger, *Ber.* ix. 404).

Dibromopyroracemic Acid, $C^8H^2Br^2O^3$, is formed when the dibromolactic acid, $C^3H^2Br^2O^3$, which Wislicenus obtained by the action of bromine on pyroracemic acid (vi. 771), is heated in a stream of chlorine. It crystallises in rather large rhombic plates melting at 93° (Ph. Clermont, *Bull. Soc. Chim.* [2], xix. 103).

Tribromopyroracemic Acid, $C^8HBr^3O^3 = CBr^3.CO.CO^3H$ (Grimaux, *Bull. Soc. Chim.* [2], xxi. 390). This acid is formed, together with the dibrominated acid, by the action of bromine on pyroracemic acid. 1 pt. of the acid and 1 pt. water are introduced into a flask with vertical condensing tube, heated in a water-bath, and 4 pts. bromine are slowly added. The contents of the flask solidify on cooling to a crystalline mass, and the formation of *small* crystals may be promoted by external cooling and stirring. The crystals are freed by the filter-pump from the mother-liquor (which also contains the dibrominated acid), mixed with a small quantity of cold water, and once recrystallised from water at 80° .

Pure tribromopyroracemic acid thus obtained forms laminae resembling naphthalene, having the composition $C^8HBr^3O^3 + 2H^2O$, and melting at 104° . It does not part with its water of crystallisation either in the air or in a vacuum, or even to the smallest amount when heated for several days at 50° – 60° , but the whole of it is given off at 100° . The dehydrated acid melts at 90° . The acid is sparingly soluble in cold, easily in hot water, also in alcohol and in ether. It decomposes quickly when boiled in aqueous solution, a dense liquid passing over with the steam, which boils above 140° , and appears to consist of bromoform. At the same time oxalic, carbonic, and hydrobromic acids are formed, together with a solid body which reduces ammoniacal silver solution. Ammonia and lead acetate also readily decompose tribromopyroracemic acid, with formation of oxalic acid. The tribrominated acid precipitates calcium salts at ordinary temperatures, and forms with silver nitrate an immediate precipitate of silver bromide. It reduces auric chloride and mercuric chloride; it is not acted on by acetyl chloride.

The same tribromopyroracemic acid is formed by the action of bromine on ordinary lactic acid, and this reaction, which is perfectly analogous to the formation of tetrabromacetone from pseudopropyl alcohol, observed by Friedel (*Compt. rend.* ix. 346), affords a further confirmation of Wichelhaus's formula for pyroracemic acid:



Compounds of Pyroracemic Acid with Alkaline Sulphites (Clewning, *J. pr. Chem.* [2], xvii. 241). 1. *Sodium salts*.—A mixture of pyroracemic acid with a recently prepared solution of normal sodium sulphite yields crystals of the salt $C^8H^8O^3Na.HSO^2Na + H^2O$, easily soluble in cold water (100 pts. water dissolve 26.6

of the dry salt). The solution is not precipitated by barium chloride, except on addition of ammonia. Strong acids liberate sulphurous acid from it. Under somewhat different circumstances, the salt $2(\text{C}^3\text{H}^3\text{O}^3\text{Na}, \text{HSO}^3\text{Na}) + 3\text{H}^2\text{O}$ was obtained in prisms several centimeters long; it is less soluble than the former salt, and does not give off its water of crystallisation so readily. Pyroracemic acid and acid sodium sulphite yield the salt $\text{C}^3\text{H}^3\text{O}^3, \text{HSO}^3\text{Na}$, which decomposes when boiled with water, giving off sulphur dioxide. It is not converted into a disodic salt by addition of the corresponding quantity of soda-ley, the mixture being rather disposed to deposit normal sodium sulphite.

2. *Potassium salts*.—A concentrated solution of normal potassium sulphite mixed with excess of pyroracemic acid deposits, after a few days, strongly refracting octohedrons of the salt $\text{C}^3\text{H}^3\text{O}^3, \text{HSO}^3\text{K}$, of which 100 pts. water at 17° dissolve 44.9 pts. Its solution when boiled gives off sulphur dioxide, and leaves a thick syrup, which, after prolonged sojourn in a vacuum over sulphuric acid, has the composition $2\text{C}^3\text{H}^3\text{O}^3\text{K}, \text{HSO}^3\text{K}$. The mother-liquor of the former salt, mixed with a large excess of normal potassium sulphite, deposited, after about a week, crystals of the salt $\text{C}^3\text{H}^3\text{O}^3\text{K}, \text{HSO}^3\text{K} + \text{H}^2\text{O}$; 100 pts. water at 17.5° dissolve 32.6 pts. of the dry salt. A mixture of acid potassium sulphite with excess of pyroracemic acid deposits, when concentrated, the salt $\text{C}^3\text{H}^3\text{O}^3, \text{HSO}^3\text{K}$; when dilute, the salt $\text{C}^3\text{H}^3\text{O}^3\text{K}, \text{HSO}^3\text{K}$.

3. *Calcium salts*.—When sulphur dioxide is passed into a mixture of dissolved and precipitated calcium pyroracemate—such as is obtained by adding levigated calcium carbonate to pyroracemic acid—till the whole is dissolved, and the solution is left to evaporate in a vacuum, the salt $2(\text{C}^3\text{H}^3\text{O}^3, \text{Ca}, \text{SO}^3\text{H}) + 3\text{H}^2\text{O}$ is obtained. This salt is very soluble in water and very stable, not being acted upon by sulphuric acid of 50 per cent.; on adding acid of 66 per cent., calcium sulphite separates out, but the odour of sulphurous acid does not become perceptible till the liquid is warmed. No precipitate is formed by barium chloride. When sulphur dioxide was passed into a clear dilute solution of calcium pyroracemate, nodular groups of granules separated, consisting of the salt $(\text{C}^3\text{H}^3\text{O}^3)^2\text{Ca} + 4(\text{C}^3\text{H}^3\text{O}^3, \text{Ca}, \text{SO}^3\text{H}) + 24\text{H}^2\text{O}$, and slender needles of the salt $(\text{SO}^3\text{H})^2\text{Ca} + 4(\text{C}^3\text{H}^3\text{O}^3, \text{Ca}, \text{SO}^3\text{H}) + 15\text{H}^2\text{O}$, which could be separated by cold water, 100 pts. water at 17° dissolving 4.1 pts. of the former and 143 pts. of the latter.

4. The *Strontium salt*, $\text{C}^3\text{H}^3\text{O}^3, \text{Sr}, \text{SO}^3\text{H} + 5\text{H}^2\text{O}$, separates as a bulky crystalline pulp on passing sulphur dioxide into a solution of strontium pyroracemate, and may be obtained in small octohedrons by recrystallisation from warm water. It is much more soluble in hot than in cold water; the solution is not decomposed by boiling, and does not form any precipitate with barium chloride; concentrated acids, however, decompose it, with evolution of sulphur dioxide.

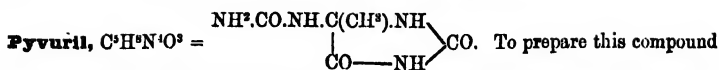
5. *Barium salt*.—When sulphur dioxide is passed into a solution of barium pyroracemate no precipitate is formed, but the solution when evaporated leaves a thick syrup which, when dissolved in boiling water, yields on cooling crystals of the salt $\text{C}^3\text{H}^3\text{O}^3, \text{Ba}, \text{SO}^3\text{H}$. This salt is very permanent; 100 pts. water dissolve 1.7 pts. of it at 17° and 7.5 pts. at 100° . Gleaning regards the formation of these compounds, and especially of the salts $\text{C}^3\text{H}^3\text{O}^3, \text{HSO}^3\text{Na}$ and $\text{C}^3\text{H}^3\text{O}^3, \text{HSO}^3\text{K}$, as demonstrative of the analogy of pyroracemic acid to the ketones and aldehydes in its behaviour to acid sulphites.

Pyroracemic Ethers. The pyroracemates of Ethyl and Methyl have been already described (vii. 1034).

Pyroracemic Glyceride, or *Pyruvin*, $\text{C}^6\text{H}^{10}\text{O}^3 = \text{C}^3\text{H}^5(\text{OH})^2(\text{OC}^3\text{H}^3\text{O}^3)$, is formed by heating tartaric acid with glycerin to a temperature higher than that which is required for the formation of glycerotartaric acids; if the mixture be heated in a retort, the pyruvin collects in fine crystals in the neck of the receiver. Pyruvin sublimes in shining laminae, melts at 78° , boils with decomposition at 242° , dissolves in alcohol, ether, carbon sulphide, and benzene, and with especial facility in chloroform, but is decomposed by water (Schlagdenhauffen, *Ann. Chim. Phys.* [4], xvi. 139).

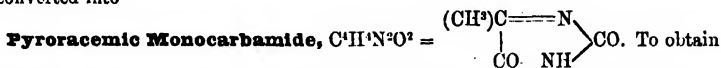
PYRORACEMIC CARBAMIDES or UREIDES (Grimaux, *Compt. rend.* lxxix. 526, 1304, 1478; lxxx. 53; *Ann. Chim. Phys.* [5], xi. 356). Pyroracemic acid and urea, heated together at 100° , yield, according to the proportions in which they are mixed, the following compounds:

Pyroracemic Dicarbamide or Pyvuril	$\text{C}^6\text{H}^{10}\text{N}^2\text{O}^3$
Dipyroracemic Tricarbamide	$\text{C}^9\text{H}^{12}\text{N}^3\text{O}^3$
Tripyroracemic Tetracarbamide	$\text{C}^{12}\text{H}^{16}\text{N}^4\text{O}^7$
Tetrapyroracemic Tetracarbamido	$\text{C}^{16}\text{H}^{16}\text{N}^4\text{O}^8$



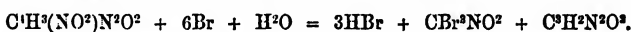
1 pt. pyroracemic acid is heated for an hour or two with 2 pts. urea, whereupon carbon dioxide is evolved, and the mass, which is at first liquid, becomes solid; and on exhausting this mass with hot alcohol, urea and ammonium pyroracemate are dissolved, while pyvuril remains behind, and may be purified by recrystallisation from about ten times its weight of boiling water, from which it separates in small shining rhombic plates.

Pyvuril may be heated to 145° without loss of weight, but when heated for several days at 155° – 160° , it is converted, with loss of about 25 per cent., into a brown-yellow amorphous substance and tetrapyracemic tetracarbamide. By boiling with baryta-water, pyvuril is resolved into urea, oxalic acid, and probably uvitic acid. Its solutions, mixed with potassium hydrate, give precipitates with the nitrates of silver and mercury. Pyvuril is resolved by dilute hydrochloric acid into urea and dipyracemic tricarbamide, and, by heating with strong hydrochloric acid, it is converted into

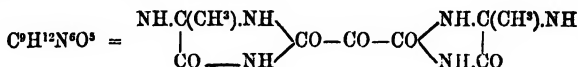


this compound in the pure state, the liquid is evaporated to dryness on the water-bath; the gummy residue is drenched with alcohol and left at rest for twenty-four hours; and the mass, which has now become crystalline and has been freed from urea by the alcohol, is recrystallised once or twice from boiling water. The monocarbamide is thus obtained as a white, very light, and indistinctly crystalline powder.

Nitropyracemic Carbamide, $C^4H^4(NO^2)N^2O^2$, is formed, together with nitrate of urea, on dissolving pyvuril in 4 or 5 pts. of moderately warm nitric acid of ordinary strength; and, on evaporating the solution to a pasty consistence, washing the residue with cold water, and crystallising it from 25 pts. of hot water, the nitrocarbamide is obtained in shining pale-yellow scales. It has a sweet taste, may be heated to 140° without loss of weight, and is converted at 160° into an amorphous substance which, by treatment with hot water, is reconverted into the original compound. The crystals decompose at 200° , and dissolve in alkalis with yellow colour, which disappears on addition of acids. The nitro-compound is quickly decomposed by heating with potash-ley; when boiled with lime- or baryta-water, it yields soluble yellow salts; the *silver salt*, $C^4H(NO^2)N^2O^2Ag^2$, and the *lead salt* form bulky jellies. On dissolving the nitro-compound in water and distilling the solution, after addition of bromine, bromopierin passes over, and oxalyl-carbamide (parabanic acid) remains:



Dipyracemic Tricarbamide,

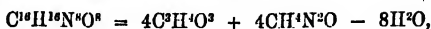


This compound is formed, by heating equal weights of urea and pyroracemic acid, as a clear liquid which gradually thickens and finally solidifies; and on exhausting the solid mass with 200 to 250 times its volume of boiling water, a solution is obtained which on cooling yields the tricarbamide in the form of a thick gelatinous mass of slender needles. It is nearly insoluble in cold water, but dissolves easily in alkalis, without, however, entering into combination with them; acids, including carbonic acid, precipitate it from its solutions as a jelly. The alkaline solutions give with silver nitrate a white precipitate; the aqueous solutions form such a precipitate only with mercury nitrate. It is decomposed by boiling with alkalis or with baryta-water, yielding, in the latter case, pyvuril, urea, and pyroracemic acid. Heated with nitric acid, it yields urea and the nitromonocarbamide above described; with pyroracemic acid at 100° , an amorphous substance.

By the action of heat on pyvuril, or by treating urea with excess of pyroracemic acid, *condensed carbamides* are formed, richer in carbon and less rich in nitrogen than the preceding; they are amorphous, insoluble in water, easily dissolved by alkalis, and reprecipitated by acids; decomposing without previous fusion when heated; not attacked by acids.

Tripyracemic Tetracarbamide, $C^{13}H^{16}N^8O^8 = 3C^4H^4O^2 + 4CH^4N^2O - 6H^2O$, formed simultaneously with dipyracemic tricarbamide, is a white powder which dissolves in alkalis without previous gelatinisation.

Tetrapyracemic Tetracarbamide,



is precipitated by acids from its solutions in alkalis as a bulky jelly which dries up to a granular mass; it is not attacked by boiling potash-ley or by nitric acid.

Tribromanhydropyvuril, $C^3H^3Br^3N^3O^2$, is formed by heating equal parts of bromopyracemic acid and urea at 100° , the mixture first liquefying and then solidifying after a few hours. By washing the mass with cold water and recrystallising it from hot water, the tribromanhydropyvuril is obtained in light needles, which melt with decomposition at 180° . It has a sharp taste, provokes sneezing, dissolves in hot water, alcohol, ether, and ether-alcohol. Its solution gives with silver nitrate a precipitate containing silver and bromine. Dibromopyracemic acid acts upon urea in the same manner as the tribrominated acid.

PYROSCLERITE (iv. 770). The following analysis, by J. Ebert, of pyrosclerite from the limestone cleft of St. Philipp, near St. Marie aux Mines, Alsace, has been published by A. Knop (*Jahrb. f. Min.* 1870, 70):

SiO ²	Al ² O ³	CaO	MgO	FeO	H ² O	
38.7	16.1	6.1	25.9	0.5	12.8	100.1

The carbonic acid present is not sufficient to allow of the whole of the lime being regarded as admixed limestone.

A rhombic silicate (possibly pyrosclerite) of greyish and occasionally bronze-yellow colour, and sp. gr. 2.558, occurring as a contact product between talc and gymnite on the Bare Hills near Baltimore, has been analysed by A. R. Leeds (*Sill. Am. J.* [3], vi. 24):

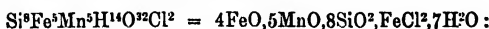
SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	Na ² O	Li ² O	H ² O
36.03	9.19	5.48	0.94	33.05	0.41		14.66 = 99.76
35.84	9.85	5.21	1.21	32.93	0.41		14.53 = 99.98

PYROSMALITE. Wöhler (*Liebig's Annalen*, clvi. 85), from three analyses made by himself, and an older analysis by Hisinger (iv. 771), gives for this mineral the following composition:

SiO ²	FeO	MnO	Fe ² O ³	Fe ² Cl ³	H ² O
36.42	22.91	22.52	5.10	9.73	3.32 = 100

and deduces therefrom the formula $(Fe^2Cl^6, Fe^2O^3) + 10(FeO, SiO^2 + MnO, SiO^2) + 8H^2O$.

E. Ludwig (*Min. Mitth.* 1875, 211) gives analyses of pyrosomalite from Nordmarken, from which he deduces the empirical formula:

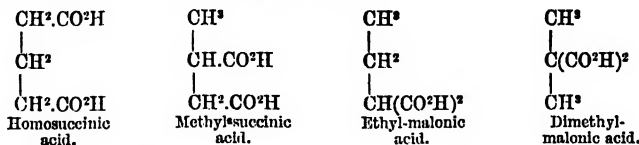


	SiO ²	FeO	MnO	CaO	MgO	H ² O	Cl	Total	O *	Residue
Analysis	34.66	27.05	25.60	0.52	0.93	8.31	4.88	101.95	1.10	100.85
Calculation	34.88	26.16	25.80	—	—	9.16	5.16			

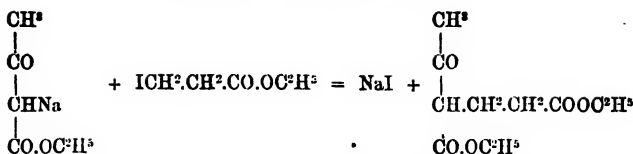
* To be deducted as equivalent to the chlorine.

PYROSULPHURIC ACID, $S^2H^2O^7 = 2SO^2, H^2O$. See SULPHUR, OXYGEN-ACIDS OF.

PYROTARTARIC ACIDS, $C^4H^4O^4$. Theory indicates the existence of four of these acids, all of which are now known, viz.:



1. **Normal Pyrotartaric, Homosuccinic, or Glutaric Acid**, $CH^2(CH^2.CO^2H)^2$. This acid, identical with the deoxyglutanic acid which Dittmar obtained (*J. pr. Chem.* [2], v. 338) by heating glutanic acid, $C^5H^8O^5$, with hydriodic acid (vii. 362), is also produced: α . By saponification of normal propylene cyanide, $CH^2(CH^2.CN)^2$, prepared by the action of potassium cyanide on normal propylene bromide in presence of alcohol (Julie Lermontoff, *Ber.* ix. 1441; Reboul, *Bull. Soc. Chim.* [2], xxv. 386). β . By treating ethyl sodaceto-acetate with ethylic β -iodopropionate, whereby ethylic aceto-glutanate is formed, according to the equation:



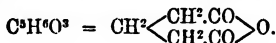
and decomposing this ether with alcoholic potash (Wislicenus a. Limpach, *Liebig's Annalen*, xcii. 128).

Glutaric acid crystallises very easily from aqueous solution in large transparent four-sided prisms, melts at 97° (Dittmar), at 97.5° (Markownikoff), at 96° (corr. Reboul) and boils at 291° (corr. 299° , Reboul), at 302° (Markownikoff).^{*} When glutaric acid (8.5 grams) is heated with bromine (21 g.) and water (10 c.c.) at 145° , it yields nothing but HBr, CO, and CO_2 ; at 118° – 120° the bromine disappears more slowly, with evolution of CO_2 and HBr, and the liquid on cooling deposits crystals of dibromosuccinic acid. With 7.2 g. glutaric acid, 18 g. bromine, and 15 c.c. water heated at 100° for ninety hours, the products are tetrabromethane and dibromoglutaric acid (Bourgoin a. Reboul, *Compt. rend.* lxxxiv. 556).

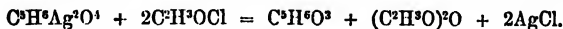
Calcium glutarate, $\text{C}^{\text{b}}\text{H}^{\text{b}}\text{O}^{\text{b}}\text{Ca} + 4\text{H}^{\text{b}}\text{O}$, crystallises in stellate groups of slender needles, more soluble in cold than in hot water. The *magnesium salt* is very soluble, and partly separates from very concentrated solutions in microscopic four-sided plates, the greater part, however, drying up to an amorphous mass; from dilute alcohol it crystallises in small needles. The *zinc salt*, $\text{C}^{\text{b}}\text{H}^{\text{b}}\text{O}^{\text{b}}\text{Zn}$, is but very slightly soluble in cold water (1 pt. in 102 pts. water at 18°), and still less in hot water. The solution prepared at ordinary temperatures deposits, when heated, microscopic rectangular plates with re-entering angles on the shorter sides of the rectangle.

Diethyl glutarate, $\text{CH}^{\text{c}}(\text{CH}^{\text{c}}.\text{COOC}^{\text{c}}\text{H}^{\text{c}})^2$, is prepared by passing hydrogen chloride to saturation into a solution of the acid in absolute alcohol, distilling, collecting the portion which goes over between 240° and 260° , freeing this distillate from unetherified glutaric acid by digestion with potassium carbonate, and redistilling. The pure ether is a colourless liquid having a disagreeable odour, a density of 1.025 at 21° , and boiling without decomposition at 236.5 – 237° (corr.) (Reboul, *Ann. Chim. Phys.* [5], xiv. 510).

Normal Pyrotartaric or Glutaric Anhydride,



When glutaric acid is slowly distilled, either alone or in contact with phosphoric anhydride, water passes over first, and afterwards, at 282° – 285° , a crystalline mass which melts at 80° – 85° , and consists of a mixture of acid and anhydride. It is difficult, however, to obtain the pure anhydride in this way, and a better product is obtained by the action of acetyl chloride in ethereal solution on silver glutarate:



Glutaric anhydride crystallises in white slender needles, melts at 56° – 57° , and boils, with decomposition, at 282° – 287° . By prolonged contact with alcohol, it is converted into ethyl-hydrogen glutarate (Markownikoff, *Ber.* x. 972, 1102).

Glutaric chloride, $\text{CH}^{\text{c}}(\text{CH}^{\text{c}}.\text{COCl})^2$, obtained by the action of 2 mol. PCl_5 on 1 mol. of the acid, is a heavy liquid having an irritating odour, boiling, with perceptible decomposition, at 216° – 218° , and converted by water into hydrochloric and glutaric acids (Reboul, *Ann. Chim. Phys.* [5], xiv. 510).

Normal Hydroxypyrotartaric Acid, $\text{C}^{\text{b}}\text{H}^{\text{b}}\text{O}^{\text{b}}$.—There are two modifications of this acid, viz.:



^{*} Markownikoff found that the acid prepared from glutaric acid boiled at 302° , whereas that prepared from propylene cyanide boiled at 215° , and he attributes the difference to some diversity in the circumstances of the distillation. As, however, the higher boiling point agrees nearly with that determined by Reboul, it may safely be regarded as nearer to the truth than the lower. According to Dittmar, the acid decomposes at temperatures above 280° into water and the anhydride.

The symmetrical modification was discovered in 1862 by Maxwell Simpson, who obtained it by heating symmetrical dichlorhydrin, $\text{CH}^2\text{Cl}.\text{CHOH}.\text{CH}^2\text{Cl}$, with potassium cyanide in alcoholic solution, and saponifying the resulting dicyanhydrin with alcoholic potash. It forms hard crystals very soluble in cold water, slightly soluble in alcohol and ether (vii. 886).

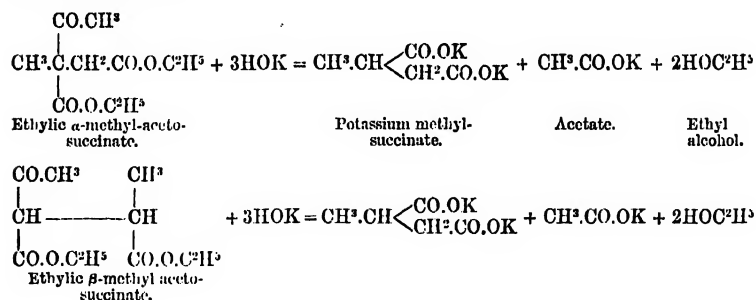
The unsymmetrical modification, called glutamic acid, obtained by the action of nitrous acid on glutamic acid, $\text{C}^5\text{H}^5\text{NO}^4$, was discovered by Ritthausen (vi. 637), and has been further examined by Markownikoff (*Liebig's Annalen*, clxxxii. 347). It may be prepared by passing nitrous gas into a solution of glutamic acid in nitric acid, or more advantageously by mixing a solution of glutamic acid in hydrochloric acid with an equivalent quantity of potassium nitrite. It is difficult to obtain in well-defined crystals. It melts at $72^\circ\text{--}73^\circ$, and solidifies, on cooling, to a clear amorphous mass. It appears to form with bases two classes of neutral salts differing in solubility.

The *zinc salt*, obtained by saturating the acid with zinc carbonate, crystallises from a syrupy solution, on standing, in transparent four-sided tables, which when dissolved in hot water are transformed into a pulverulent sparingly soluble salt. From a hot saturated solution it crystallises in nodules agreeing in composition with the formula $\text{C}^5\text{H}^5\text{O}^5\text{Zn} + 3\text{H}^2\text{O}$. The *magnesium salt*, $\text{C}^5\text{H}^5\text{O}^5\text{Mg} + 4\text{H}^2\text{O}$, obtained in the same manner as the zinc salt, is sparingly soluble in cold water, and crystallises from hot solutions in transparent microscopic rhombic tables.

Glutamic acid, when heated to 190° , is converted into an anhydride, which dissolves in water, reproducing the acid. By reduction it yields glutaric acid (p. 1721).

2. Ordinary Pyrotartaric or Methyl-succinic Acid, $\text{CH}^3.\text{CH} \begin{smallmatrix} \text{COOH} \\ \text{CH}.\text{COOH} \end{smallmatrix}$

This acid, originally obtained by the dry distillation of tartaric acid (iv. 771), is also produced: (1). By the action of boiling aqueous potash on the ethylic ethers of α - and β -methylacetosuccinic acid, which are obtained in the same way as the corresponding ethers of α - and β -ethylacetosuccinic acid, using methyl instead of ethyl iodide in the case of the α -ether, and ethylic α -bromopropionate instead of the α -bromobutyrate in that of the β -ether (see ACETO-ACETIC ETHERS, pp. 15, 16). The reactions by which methylsuccinic acid is formed from these ethers are represented by the following equations:



(Conrad, *Liebig's Annalen*, clxxxvii. 217; Kressner, *ibid.* excii. 135).

(2). By the action of boiling aqueous potash on the dicyanide obtained by heating allyl iodide in a sealed tube with 2 mols. potassium cyanide and a little alcohol (Claus, *Ber.* v. 612; viii. 100).

Electrolysis.—When a concentrated solution of pyrotartaric acid is electrolysed, hydrogen appears at the negative pole, and oxygen, mixed with CO and CO^2 , at the positive pole. A solution of potassium pyrotartrate when electrolysed deposits on the positive pole crystals of the acid salt, which disappear after some time, the solution then containing free pyrotartaric acid. Solutions containing excess of alkali give off considerable quantities of gas, consisting of carbon dioxide, carbon monoxide, and oxygen (Reboul a. Bourgoin, *Compt. rend.* lxxxiv. 1231).

Reaction with Bromine.—When pyrotartaric acid is treated with bromine (1 mol.) in a closed vessel at 120° , the chief product obtained is bromocitrapyrotartaric anhydride, together with very small quantities of an apparently monobrominated acid. With 2 mols. bromine, the product consists of bromocitraconic anhydride. *Bromocitrapyrotartaric anhydride* melts at $104^\circ\text{--}105^\circ$, has a sp. gr. of 1.935 at 23° , dissolves readily in alcohol and ether, sparingly in chloroform, and when heated with water in sealed tubes at 130° yields carbon dioxide and allylone. When pyrotartaric acid is heated with 4 mols. bromine at $130^\circ\text{--}132^\circ$, carbon dioxide is given off, and a tetra-

bromide of acetylene, $C^2H^2Br^4$, is formed, which has a density of $\cdot 2\cdot 93$ at 0° , boils with partial decomposition at about 200° , and solidifies at -17° , whereby it is distinguished from the other known acetylene tetrabromides, one of which remains liquid at -17° (p. 35), while the other is solid at ordinary temperatures, and melts at $54\cdot 5^\circ$ (Bourgoin, *Ann. Chim. Phys.* [5], xii. 419).

Bromopyrotartaric acids, $C^2H^2BrO^4$.—The crystalline forms of these isomeric acids (vi. 49, 980) have been determined by Arzruni (*Zeitschr. Kryst.* i. 439). *Citra-bromopyrotartaric acid* crystallises in the monoclinic system with the axial ratio $a : b : c = 0\cdot 7504 : 1 : 1\cdot 1175$; $\beta = 84^\circ 5'$. Principal forms, OP , $\infty R\infty$, ∞P , $-P$, $+P$, $R\infty \infty P\infty$. Angle $\infty P : \infty P\infty = 36^\circ 53'$. Cleavage perfect parallel to $\infty P\infty$ and $\infty P\infty$. Plane of optic axes perpendicular to the plane of symmetry. *Itabromopyrotartaric acid* is also monoclinic. Axial ratio $a : b : c = 0\cdot 2914 : 1 : 0\cdot 4101$; $\beta = 65^\circ 38'$. Forms ∞P , $P\infty$, $\infty P\infty$.

3 and 4. **Ethylmalonic and Dimethylmalonic acid** have already been described as MALONIC ETHERS.

The following tabular view of the properties of the isomeric pyrotartaric acids is given by Markownikoff (*Liebig's Annalen*, clxxxii. 324):

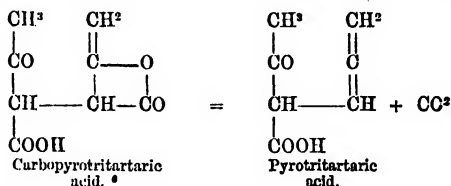
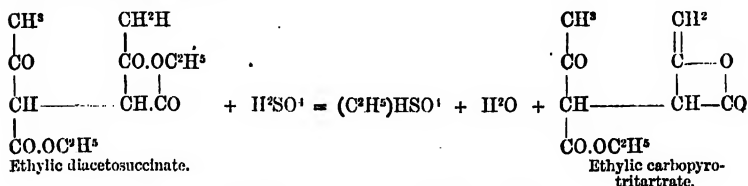
Acid.	Glutaric or Homosuccinic acid	Pyrotartaric or Methyl-succinic acid	α -Isopyrotartaric or Ethyl-malonic acid	β -Isopyrotartaric or Dimethyl-malonic acid
-	Large flat plates, easily soluble in water; melts at 97° ; boils, almost without decomposition, at 302° .	Four-sided prisms; easily soluble in water; melts at 112° ; boils at about 200° , being converted into the anhydride.	Short four-sided prisms, easily soluble in water; melts at $111\cdot 5^\circ$; decomposes without subliming, at 160° .	Short four-sided prisms, easily soluble in water; melts, with decomposition, at 170° ; sublimes at 120° .
Calcium salt.	Easily soluble in cold, less easily in hot water. Crystallises with difficulty.	Somewhat sparingly soluble in cold water. Crystallises with $2H^2O$.	Slightly soluble in hot, easily in cold water. Crystallises in prisms with $11H^2O$.	Less soluble in hot than in cold water. Crystallises in nodules.
Zinc salt.	Microscopic twins, soluble in 102 pts. water at 18° .	Easily soluble.	Microscopic six-sided plates. Soluble in 456 pts. water. Contains $2\frac{1}{2}H^2O$.	Like the α -salt. Dissolves in 106 pts. water. Contains $311H^2O$.
Lead salt.		White precipitate.	White precipitate, becoming granular on boiling.	White precipitate, converted on boiling into shining scales.

PYROTEREBIC ACID. See TEREBIC ACID.

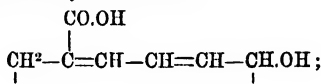
PYROTRITARTARIC or UVIC ACID, $C^4H^6O^7$. This acid, which Wislicenus a. Stadnicki obtained, together with pyrotartaric acid, by the dry distillation of tartaric acid (vi. 981), is also produced: 1 By heating pyroracemic acid with a quantity of barium hydrate less than sufficient to neutralise it. 40 to 50 grams of pyroracemic acid and 25 to 30 grams of crystallised barium hydrate are boiled together for six hours in a flask with vertical condenser and then left to cool, whereupon the liquid acquires a dark-red colour and deposits uvic acid (7 p. c. of the pyroracemic acid) in small interlaced needles, while pyrotartaric acid remains dissolved, together with acetic acid and small quantities of other acids not determined (Böttiger, *Liebig's Annalen*, clxxxii. 239). 2 By the action of dilute sulphuric acid on ethylic diacetosuccinate. 20 grams of this ether are boiled with 150 g. dilute sulphuric acid (1 : 10) in a reflux apparatus as long as carbon dioxide continues to be evolved, after which the liquid is distilled in a current of steam. Alcohol then passes over, together

with the water, and an oil which smells like anise, and after repeated distillation boils at 208°–209°. This oil is the ethylic ether of pyrotritartaric acid, and yields the acid by saponification. The residue of the distillation contains carbopyrotritartaric acid, $C^8H^8O^8 = C^7H^8O^8 + CO^2$, partly in the free state, partly in the form of ethylic ether (G. H. Harrow, *Chem. Soc. J.* xxxv. 425).

The formation of these acids from ethylic diacetosuccinate may be represented by the following equations:



Bötttinger represents uvic acid by the formula:



but Harrow points out that this formula will not explain the formation of the acid from ethylic diacetosuccinate, and, moreover, that Wislicenus a. Stadnicki have shown that uvic acid does not contain a second hydroxyl-group.

Uvic acid is nearly insoluble in cold water, but dissolves to a considerable amount in boiling water; it is soluble also in ether, and crystallises therefrom in prismatic needles melting at 135° (Harrow). According to Bötttinger, it separates from boiling water in crystals having a vitreous lustre, sparingly soluble in cold water, melting at 133°, and resolidifying at 126°. It volatilises with vapour of water, and sublimes in smooth rectangular prisms, joined together like steps, and melting at 134°. On mixing a very small quantity of it on a watch-glass with 2 drops of fuming hydrochloric acid, then heating slightly, adding about 6 drops of strong sulphuric acid, and again gently warming, a fine cherry-red colour is produced (Harrow).

Uvic acid is monobasic. Its *sodium salt*, $C^7H^7NaO^8$, is a white crystalline mass, easily soluble in water (Harrow). The *silver salt*, $C^7H^7AgO^8$, is thrown down by silver nitrate from a solution of the acid neutralised with soda or ammonia, as a white precipitate which quickly turns greyish-yellow on exposure to light, but may be converted by crystallisation into small transparent prisms possessing greater stability. The *barium salt*, $(C^7H^7O^8)^2Ba + 5H^2O$, prepared from the acid by means of barium hydrate and carbon dioxide, forms indistinct crystalline geodes. The *calcium salt*, $(C^7H^7O^8)^2Ca + 3H^2O$, crystallises in radiate needles. The *zinc salt*, $(C^7H^7O^8)^2Zn + 4H^2O$, is more readily soluble in cold than in boiling water. It is prepared by nearly neutralising a moderately warm solution of the acid with zinc oxide, and leaving it for some time in the exsiccator; the solution then first deposits a small quantity of the free acid, and afterwards the zinc salt in large round geodes. With *mercurous nitrate*, a solution of uvic acid forms a white precipitate which is not altered by boiling with water (Bötttinger).

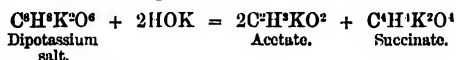
The *ethylic ether*, $C^8H^8O^8.C^2H^5$, is obtained, as above mentioned, by boiling ethylic diacetosuccinate with sulphuric acid, also by decomposing the silver salt with ethyl iodide. When purified by repeated distillation, it melts at 208°–209° (Harrow).

Carbopyrotritartaric Acid, $C^8H^8O^8$, remains, as above stated, as the residue of the distillation in the preparation of pyrotritartaric acid, partly in the free state, partly as ethylic ether, which may be saponified by prolonged boiling with dilute sulphuric acid. The acid crystallises from boiling water, in which it is moderately soluble, in long very slender needles, which melt at 230°–231°, especially in presence

of a small quantity of sulphuric acid. It is nearly insoluble in cold water. The sodium salt, $C^8H^7NaO^4 + 3H^2O$ (?), crystallises from water in long needles. It dissolves easily in water, sparingly in alcohol, and, like the ammonium salt, has a persistent bitter taste. The silver salt, $C^8H^7AgO^4$, is obtained as a dense precipitate, and crystallises from boiling water in slender needles, turning grey when exposed to light. When heated, it yields carbopyrotritartaric and pyrotritartaric acids. The ethylic ether, $C^8H^7O^4C^2H^5$, forms needles melting at $80^\circ-81^\circ$.

Carbopyrotritartaric acid is resolved by heat into pyrotritartaric acid and carbon dioxide. It is neutralised by 1 equivalent of sodium hydroxide, NaOH, and is therefore monobasic; but, if heated for some time with 2 mols. sodium hydroxide, it yields a solution from which silver nitrate throws down no longer a brown precipitate of silver oxide, but a white precipitate of a *diargentic salt*, having the composition $C^8H^4Ag^2O^6$. The acid reprecipitated from this salt by dilute nitric acid is unaltered carbopyrotritartaric acid. From this result, and the fact that carbopyrotritartaric acid splits up on heating into CO^2 and pyrotritartaric acid, which undoubtedly contains a carboxyl-group, it may be inferred that it belongs to the class of etheric anhydrides.

Carbopyrotritartaric acid is not altered by boiling with strong aqueous potash, even for several hours, but by fusion with potassium hydroxide, it is resolved into acetic and succinic acids, according to the equation :



(Harrow, *Chem. Soc. J.* xxxv. 435).

PYROUSNIC ACID, $C^{12}H^{12}O^3$. See USNIC ACID.

PYROVANADATES. See VANADIUM.

PYROXANTHIN, $C^{13}H^{12}O^3$. The action of bromine on this substance (contained in crude wood-spirit, and produced by the action of potash on one of the constituents of wood-tar oil (iv. 776 *) has been examined by H. B. Hill (*Ber.* xi. 456). When dissolved in carbon sulphide and treated with a solution of bromine in the same liquid, it is slowly converted into dibromopyroxanthin tetrabromide, $C^{13}H^{10}Br^2O^3.Br^4$, which crystallises from solution in benzene in small white triclinic needles, and is converted by boiling with absolute alcohol and metallic antimony into dibromopyroxanthin, $C^{13}H^{10}Br^2O^3$, soluble in alcohol and crystallising therefrom in bright yellow well-defined monoclinic needles; this latter compound is not produced by the direct action of bromine on pyroxanthin. Pyroxanthin boiled with zinc-dust and acetic acid containing a little alcohol is converted into hydroxyroxanthin.

PYROXENE or **AUGITE**, $R''SiO^3$. The following analyses of augites have been made by C. Doelter (*Min. Mitth.* 1877, 279): 1. Black augite from Vesuvius: crystals of the form $\infty P . \infty P \infty . \infty R \infty . P$, from a sanidin bomb. 2. Dark green from Vesuvius: crystals of the same form, likewise from a bomb. 3. Yellow augite from Vesuvius: crystals having the form $2P$, together with those above mentioned; also from a bomb. 4. Simple crystals and twins of the ordinary form from Lipari. 5. Simple crystals and twins of the ordinary form from a basaltic lava from Cuglieri in Sardinia. 6. Augite in prismatic crystals from Greenwood furnace. 7. Augite of the combination $\infty P . \infty P \infty . \infty P \infty . 0P . \frac{1}{2}P \infty$, from the melaphyre of the Bufaureberg, South Tyrol. 9. Dark green, and 10. Colourless portions of a variously coloured diopside crystal from Ala:

	SiO ^a	CaO	MgO	FeO	FeO ^a	Al ² O ^a	Sp. gr.
1.	46.95	19.02	16.04	4.09	4.47	9.75 = 100.32	3.275
2.	51.01	20.80	16.58	3.16	3.51	4.84 = 99.90	3.203
3.	50.41	22.75	12.92	6.78	1.09	6.07 = 100.02	3.298
4.	48.45	20.30	14.35	6.94	3.57	6.68 = 100.29	3.225
5.	46.65	21.09	13.60	5.05	6.32	8.61 = 100.32	3.299
6.	49.18	20.62	16.83	2.55	5.05	5.09 = 99.32	3.295
7.	49.01	20.01	14.55	7.74	3.77	5.09 = 100.17	3.299
8.	44.76	24.90	13.65	2.09	5.01	10.10 = 100.51	3.979
9.	54.28	25.04	17.30	1.91	0.98	0.51 = 100.02	
10.	54.74	26.03	17.02	2.91	—	— = 100.70	

From these analyses, Doelter endeavours to decide between the views of Rammelsberg and Tschermak respecting the constitution of aluminiferous augites, the former

* The empirical formula $C^8H^4O^3$ there given is erroneous; it should be C^8H^4O .

regarding them as isomorphous mixtures of RSiO_3 with Al_2O_3 and Fe_2O_3 , whereas the latter assumes for the admixture of aluminium and sexvalent iron, the formulæ $\text{MgAl}_2\text{SiO}_6$ and $\text{MgFe}_2\text{SiO}_6$. Doelter concludes that all his analyses conform to the fundamental condition of Tschermak's hypothesis, inasmuch as, for all the aluminiferous augites analysed, $\text{Ca} < \text{Mg} + \text{Fe}$, the difference being considerable in most cases, small only in No. 3. Doelter further shows that, with the exception of Nos. 3, 5, and 7, the analytical results may be represented by the formula $x(\text{MgCaSi}_2\text{O}_6) + y(\text{FeCaSi}_2\text{O}_6) + x'(\text{MgFe}_2\text{SiO}_6) + y'(\text{MgAl}_2\text{SiO}_6)$, thus;

	MgCaSi ² O ⁶	FeCaSi ² O ⁶	MgFe ² SiO ⁶	MgAl ³ SiO ⁶		
in 1 = 10	:	2	:	1	:	3
„ 2 = 16	:	2	:	1	:	2
„ 4 = 12	:	4	:	1	:	3
„ 6 = 19	:	2	:	2	:	3
„ 8 = 8½	:	5	:	1	:	1

Varieties of Pyroxene.—A. R. Leeds (*Zeitschr. f. Kryst.* ii. 642) has analysed hypersthene (No. 1) and diallage (No. 2) from the norites of the Adirondacks Mountain, New York: sp. gr. 3.459:

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	H_2O	
50.33	0.07	3.36	1.03	19.40	0.71	2.77	21.40	1.14	= 100.21
46.28	0.59	7.38	2.21	14.80	—	18.78	8.91	1.115	= 100.065

A brown pyroxene (A), nearly related to bronzite, and a chrome-diopside (B), from the olivine-nodules of the Lützelberg, Kaiserstuhl range (p. 1435), have been analysed by A. Knop (*Jahrb. f. Min.* 1877, 697). The bronzite contained about 1.5 per cent. chrome iron ore mechanically mixed, being itself free from chromium whereas in the chrome-diopside no such admixture was perceptible:

SiO_2	X *	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	
52.50	2.00	2.29	—	6.07	—	32.23	4.35	= 99.44
51.89	2.30	4.76	1.09	4.40	0.54	15.47	19.73	= 100.18

* Residue left on dissolving the separated silica in soda-ley; possibly containing niobic and titanate acids, which, however, could not be detected, owing to the small quantity of the available material.

K. Oebbecke (*Inaug. Dissert.* Würzburg, 1877, 21; *Jahrb. f. Min.* 1877, 844) found in chrome-diopside from the palaeopierite of the Black rocks, Nassau:

SiO_2	Al_2O_3	Cr_2O_3	FeO	MgO	CaO	Sp. gr.
50.443	5.105	1.403	9.696	17.418	14.629	= 98.694 3.202

Salite from Albrechtsberg in Lower Austria has been analysed by E. v. Ramberger. It occurs in granular limestone, forming groups of crystals of various length up to 12 centimeters. A. analysis. B. calculation from the formula $\text{MgCaSi}_2\text{O}_6$:

	SiO_2	Al_2O_3	FeO	CaO	MgO	Sp. gr.
A.	55.60	0.16	0.56	26.77	18.34	= 101.43 3.167
B.	55.56	—	—	25.92	18.52	= 100

Fassaite, from the Fassa and Fleims valleys, has been analysed by C. Doelter (*Jahrb. f. Min.* 1877, 647) with especial attention to the separation of the two oxides of iron.

1. Pure crystals from the Toal della Foga. 2. Crystallo-granular variety from the same locality. 3. Grass-green crystals from the northern declivity of the Mal Inverno:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	H_2O	
1.	43.81	9.97	7.01	1.52	12.51	25.10	0.51	= 100.43
2.	44.06	10.43	5.91	1.67	13.10	25.20	0.15	= 100.52
3.	41.97	10.63	7.36	0.55	10.29	26.60	2.70	= 100.10

These analyses show that fassaite is more nearly related to the aluminiferous augites than to diopside, but that it is specially characterised by the predominance of ferric over ferrous oxide, and of lime over magnesia.

PYRRHOTIN, FeS_2 . *Magnetite Pyrites. Pentlandite.*—This mineral occurs, together with native iron, in the dolerite of Greenland, in masses varying from small grains to blocks of considerable size. It differs in appearance and structure from troilite, which is found in large nodules in meteorites. Its analysis gave:

S	Fe	Ni	Co	Cu	Sp. gr.
38.38	58.48	1.05	0.55	1.58	= 100.04 4.46

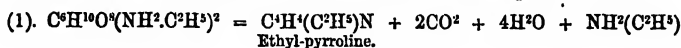
It is lighter than troilite (sp. gr. 4.9) and much more magnetic (J. L. Smith, *Ann. Chim. Phys.* [5], xvii. 452).

PYRROLINE (commonly called *Pyrrrol*), $C^4H^5N = NH$ $\begin{matrix} \text{CH}-\text{CH} \\ \parallel \\ \text{CH}-\text{CH} \end{matrix}$ (see FUR-

FURAL-DERIVATIVES, p. 836). This base is formed in considerable quantity when diethylamine is passed through a tube heated to low redness (C. A. Bell); in small quantity, together with ammonium cyanide, when acetylene containing small quantities of ethylene is passed, together with ammonia, through a red-hot tube (Dewar, *Proc. Roy. Soc.* xxvi. 65).

Acetyl-pyrroline, $C^4H^4(C^2H^3O)N$, formed by the action of acetic anhydride on pyrroline, is a liquid boiling at 133° . It is not attacked by ethyl iodide or by alkali-metals, and therefore does not contain an NH^2 -group; in other words, the nitrogen-atom in it is directly associated with only 1 atom of hydrogen, as represented by the above formula. Bromine converts it into dibromacetyl-pyrroline, $C^2H^3O.N(CH-CHBr)^2$ (R. Schiff, *Ber.* x. 1500).

Alcoholic or Alkyl Derivatives of Pyrroline, and Alkyl-pyrrolamides (C. A. Bell, *Ber.* x. 1861; xi. 1810).—When the mucates of primary amines of the fatty series are heated in a paraffin-bath, there are produced: (1). *Alkyl-pyrrolines*, and (2). *Alkylamides of the mono- and di-carboxylated derivatives of these pyrrolines*. Ethylamine mucate, for example, is decomposed as follows:



and the nascent ethylamine resulting from the first reaction acts further on the ethylamine mucate, producing triethyldicarboxypyrrolamide, $C^2H^3NO^2$, thus:



Methylamine mucate undergoes a change similar to that represented in the last equation, but the amylamine salt is apparently decomposed as in (1) and (2).

Methyl-, Ethyl-, and Amyl-pyrroline are colourless liquids boiling at 112° – 113° , 131° , and 180° – 184° respectively (pyrroline boils at 133°). The first two resemble pyrroline; the last has a powerful and characteristic odour. They dissolve in strong acids, and exhibit the pyrroline reactions with fir-wood, mercuric chloride, &c. When boiled with strong hydrochloric acid they do not, however, deposit any solid substance as pyrroline does. Potassium does not act on them; whereas with pyrroline, hydrogen is evolved, and potassium-pyrroline, C^4H^4KN , is formed. According to Lubarin (*Zeitschr. f. Chem.* [2], v. 399), ethyl iodide reacts with potassium-pyrroline, forming an ethyl-pyrroline boiling at 155° – 175° , and having peculiar properties. This, however, is not the case, the product of the reaction being the ethyl-pyrroline described above.

Dimethyl-, Diethyl-, and Diamyl-carbopyrrolamide are beautifully crystalline bodies, melting at 89° – 90° , 43° – 44° , and 77° respectively. Heated at 120° with strong alcoholic potash, the first two yield fatty amines and *methyl- and ethyl-carbopyrrolic acids*, $C^4H^3(CH^3)N.COOH$ and $C^4H^3(C^2H^3)N.COOH$, melting at 135° and 78° respectively.

The third amide, however, only gives potassium carbonate, amylamine, and amyl-pyrroline, the corresponding acid being probably very unstable. Methyl- and ethyl-carbopyrrolic acids are also unstable, a solution of the latter in water behaving like supersaturated carbonic acid water, and rapidly giving off carbon dioxide in contact with rough surfaces. Dilute acids, boiling water, and sublimation also decompose these acids; their salts are generally very soluble.

Triethyl-dicarboxypyrrolamide (from reaction 3) is crystalline and very stable, and melts at 229° – 230° . Strong alcoholic potash at 130° decomposes it into ethylamine and *ethyl-dicarboxypyrrolic acid*, $C^4H^2(C^2H^3)N(COOH)^2$. This acid sublimes without melting at 250° , partially decomposing into pyrroline and carbon dioxide. It is quite insoluble in water. Weak acids do not act on it: strong acids slowly decompose it.

Boiling with dilute hydrochloric acid slowly dissolves ethyl-pyrroline, forming an insoluble amorphous base, which yields soluble uncrystallisable salts, and possibly has the composition $C^4H^2N^2O^2$, being formed by the reaction:



Bromine-water produces with ethyl-pyrroline a *substitution-product*, $C^4Br^2N.C^2H^3$, melting at 90° . With diethyl-carbopyrrolamide it forms a substitution-product, $C^4Br^2N(C^2H^3)CO.NH.C^2H^3$, and a soluble crystallisable oxidation-product having acid

characters and, probably, the constitution $C^4Br^2O(OH).CO.NH.O^4H^1$. The dimethyl-amide yields similar bodies. In no case was an addition-product obtained analogous to Schiff's dibromacetylpyrroline (p. 1728).

The mucates of secondary and tertiary amines do not yield derivatives of pyrroline by distillation, but give off nearly the whole of their bases in the free state, leaving tarry residues. This fact, and the indifference of the alkyl-pyrroline bases to potassium and acid chlorides, confirm Baeyer's pyrroline formula above given. During the distillation of ammonium mucate, pyrroline is probably formed by the action of ammonia on two of the hydroxyl-groups of the mucic acid, water and the imide-residue (NH) being produced, while one of the carboxyl-groups may remain attached to the pyrroline-nucleus, and so give rise to carbopyrrolamine. When the mucates of the fatty amines are decomposed, one or both of the carboxyl-groups may remain attached as shown above.

Pyrroline and some of its homologues from bone-tar have quite recently been examined by Weidel and Ciamician (*Ber.* xiii. 65-85). The tar was several times distilled, then treated with acids to remove amine-bases, and the remaining oil was separated by repeated fractional distillation into three portions, boiling between 98° and 150° ; 150° - 220° ; and 220° to above 360° . Pyrroline was obtained from the first fraction, together with toluene, ethyl-benzene, and several acids and nitrils of the fatty series; while the second fraction yielded homologues of pyrroline represented by the empirical formulae C^5H^7N and C^6H^9N . (For the methods of separating all these bodies, see *Tab.*)

Pyrroline thus prepared is a perfectly colourless, highly dispersive liquid, which, when quite pure, remains colourless for several days; it has a sp. gr. of 0.9752 at 12.5° , and boils under a pressure of 7465 mm. at 126.2° . This last is the only property in which it differs from the pyrroline obtained by Anderson, who found it to boil at 133° (iv. 783); in spite of this difference, however, Weidel and Ciamician regard their pyrroline as identical with that obtained by Anderson.

The second of the above-mentioned fractions (b. p. 150° - 220°) was found to contain two substitution-derivatives of pyrroline, represented empirically by the formulae C^5H^7N and C^6H^9N . The first of these, called homopyrroline, is a colourless oil which smells like chloroform, and boils at 145.5° under a pressure of 742.8 mm. When exposed to air and light, it changes more quickly than pyrroline, but is less readily acted on by acids, being merely converted into a viscid resinous mass, whereas pyrroline is strongly attacked by acids, and converted into a solid brittle resin. It unites with mercuric chloride, forming a white curdy-looking compound.

Homopyrroline has the same empirical composition as Bell's methyl-pyrroline (p. 1728), but differs from it considerably in boiling point, methyl-pyrroline boiling at 112° - 113° . Moreover, the mode of formation of the latter shows that the methyl-group in it takes the place of the hydrogen in the NH -group, whereas in homopyrroline the CH^3 -group is not united directly to the nitrogen, but takes the place of one of the hydrogen-atoms in the C^4H^4 -group, inasmuch as it is converted into an acetyl-derivative, $C^4H^3(CH^3)N-C^2H^3O$, by prolonged contact with acetic anhydride in presence of sodium acetate.

The oil boiling at 165° has the composition C^6H^9N , and may be provisionally formulated as dimethyl-pyrroline, $C^4H^2(CH^3)^2N$. It has an unpleasant biting odour, without the sweetish after-scent of homopyrroline. It unites with mercuric chloride, forming a white insoluble compound. It is very slowly attacked by acids, forming soft red masses not obtainable in definite form. It forms an acetyl-derivative, and therefore has both the methyl-groups included in the C^4H^4 nucleus, the formula of that derivative being $C^4H^2(CH^3)^2N(C^2H^3O)$. Acetyl-dimethylpyrroline is a thickish, and at first colourless liquid, which is not quite insoluble in water, and does not solidify at -20° . It has a mild odour like that of bitter almond oil, becomes dark-coloured on standing, and after a certain time solidifies. By boiling with potash it is resolved into its constituents.

A small fraction was obtained boiling above 165° , and probably containing still higher homologues of pyrroline.

Anderson described under the name 'Pyrrol-red' a substance having the composition $C^2H^4N^2O$, and formed according to the equation $3C^4H^2N + H^2O = C^2H^4N^2O + NH^3$. Wiedel and Ciamician have tested this equation, and found it correct so far as regards the quantity of ammonia evolved; but they have not been able to obtain the pyrrol-red of constant composition, as it continually absorbs oxygen during washing and drying, changing colour at the same time.

The following table shows the distinguishing characteristics of pyrroline, and of homopyrroline, methyl-pyrroline, ethyl-pyrroline, and dimethylpyrroline.

Characters of Pyrroline and its Homologues.

	Pyrroline, C^4H^5N	Homo- pyrroline, $C^4H^5(CH^3)NH$	Methyl- pyrroline, $C^4H^4N(CH^3)$	Dimethyl- pyrroline, $C^4H^3(CH^3)^2NH$	Ethyl- pyrroline, $C^4H^3N(C^2H^5)$
Boiling point	126-2°.	145-5°.	112°-113°.	165°.	131°.
Action of: HCl.	Converted, with great rise of tem- perature, into a brit- tle resin.	Very slowly converted into a soft resin.	Unaltered.	Converted, after pro- longed boil- ing, into a soft resin- ous mass.	Remains unaltered.
HgCl ₂ .	White precipitate.		—	White pre- cipitate.	
KOH.	—	Unaltered.	Resolved into pyrroline and methyl alcohol.	Unaltered.	
$(C^2H^5O)^2O$.	Forms an acetyl-deri- vative melt- ing at 90° (R. Schiff).	Forms an acetyl-deri- vative soli- difying be- low 0° and melting at 4°-6°.	No action.	Forms an acetyl-deri- vative re- maining liquid at -20°.	No action.

Q.

QUARTZ. *Occurrence and Formation.*—Quartz has been found, together with iron-glance, in the clefts of a trachytic lava from Lipari, in small crystals exhibiting all the marks of volcanic sublimation (G. vom Rath, *Pogg. Ann.* cxlvii. 279).

Th. Hübener (*Pogg. Ann.* cl. 643), on treating lignite from Göllitz with potassium chlorate and nitric acid, and then with ammonia and alcohol, found in the residue a number of small quartz-crystals (about 3 grams from 1 kilo. of the lignite). He attributes their formation to the action of humic acid produced in the lignite on a solution of silicates which had penetrated into it. Direct experiments made with the view of obtaining quartz by prolonged digestion of humic acid with silicates, yielded, however, merely negative results.

Quartz may be formed from amorphous silica and from tridymite by the agency of sodium tungstate. For this purpose, silica and fused sodium tungstate are alternately heated and cooled between the temperatures 800° and 950°. The silica, when heated, combines with the soda, but on cooling it is precipitated by the tungstic acid, at first as tridymite, but below 850° as quartz. The amorphous silica disappears after several hours of alternate heating and cooling, being replaced by thin plates of tridymite, amongst which are very small crystals of quartz. The number and size of the latter increase considerably if the action of the fused salt be long continued. The crystals have the density and polyhedral forms characteristic of quartz, different forms being obtained according to the method of preparation adopted (Hautefeuille, *Compt. rend.* lxxxvi. 1133, 1194).

Quartz as Pseudomorph after Crocidolite.—The brown fibrous quartz from the Orange River, analysed by Klaproth is a mixture of pure white fibrous quartz with göthite ($Fe^2O^3.H^2O$), which may be dissolved out by hydrochloric acid. Blue fibrous quartz is essentially a mixture of white fibrous quartz with crocidolite. Both varieties are pseudomorphs after crocidolite, the brown being the product of a slow and complete transformation, the blue of an incomplete and rapid transformation. The amount of alteration in each case is shown by the following analyses:

Transformation of Crocidolite into Quartz.

	Asbestos-like crocidolite from the Cape. Stromeyer	Brown fibrous quartz. F. Wibel	Blue fibrous quartz. F. Wibel
SiO ₂	50·81	57·46	97·27
FeO	33·88	Fe ₂ O ₃ 37·56	FeO 1·67
MnO	0·17	—	—
MgO	2·32	—	—
CaO	0·02	—	0·15
Na ₂ O	7·03	—	0·15
H ₂ O	5·58	5·15	0·76
	99·81	100·17	100·00

In the formation of the brown fibrous quartz, the decomposition of the crocidolite mass appears to have been accompanied by an almost simultaneous washing out of the soda, magnesia, &c., and by an oxidation and hydration of the ferrous oxide. The 33·88 p. c. FeO of the original crocidolite is exactly equivalent to the 37·56 p. c. Fe₂O₃ of the brown fibrous quartz. This shows that no iron has been carried away by the decomposing liquid, the whole of it having been oxidised *in situ*, and deposited as goëthite, Fe₂O₃·H₂O; and consequently that the circulation of the decomposing liquid and of the products of decomposition must have been very slow. This slow decomposition, indeed, has enabled the delicate fibres of crocidolite, while undergoing so complete a change of composition, to retain their form instead of being converted into a dense structureless mass of quartz. On the other hand, in the more rapid action which has produced the blue fibrous quartz, nearly all the ferrous oxide has been carried away, together with the other monoxides, leaving quartz together with about 2·5 per cent. of unaltered crocidolite.

These conclusions are confirmed by the microscopic examination of thin sections of the two varieties. The brown variety exhibits, both in longitudinal and in transverse sections, a complete and tolerably uniform impregnation with ferric hydrate, each individual fibre appearing more or less brown. In the blue mineral, on the other hand, a longitudinal section exhibits a white homogeneous matrix traversed by blue or sometimes brownish fibres, with sharp edges, running parallel to one another at various distances, and of various diameters; and in accordance with this, the transverse section appears as a snow-white substance dotted with dark points. Under the polarising microscope, the white mass exhibits double refraction, with a brilliant play of colours.

The quartzes which accompany crocidolite in a few other localities (Golling in Salzburg, Rudka in Moravia, &c.) must also be regarded, not as primary quartzes coloured by crocidolite, but likewise as secondary products resulting from an incomplete but very rapid decomposition of that mineral. The same is true with regard to the blue iron ore of Klaproth. Quartz, indeed, in spite of its prismatic habit, appears to be incapable of *originally* assuming the fibrous form of aggregation.

On the crystalline forms of Quartz, from various localities, see *Jahrb. f. Min.* 1874, 81, 113, 190; 1875, 415; 1876, 264; *Jahresh. f. Chem.* 1874, 1243; 1875, 1205; 1876, 1226.

On Quartz-diorite from Yosemite, see A. Schmidt (*Jahrb. f. Min.* 1878, 716; *Chem. Soc. J.* 1879, 512). Quartz-hornblende andesite from Wöllan in Styria; R. v. Drascho (*Jahrb. f. Min.* 1873, 768; *Jahresh. f. Chem.* 1873, 1219).

QUASSIA. Goldschmidt a. Weidel (*Wien. Akad. Ber.* lxxiv. 389), by exhausting the bark and wood of *Quassia amara* with water, obtained a yellow resinous body from which they did not succeed in separating the crystalline *quassin* described by Winckler and afterwards by Wiggers (v. 2). The resin darkens in colour on exposure to the air, and splits up into acetic and protocatechuic acids when fused with potash.

QUEBRACHO. The wood of the *Quebracho colorado*, an Anacardiaceous tree growing in the northern part of the Argentine Republic, has a sp. gr. of 1·11 to 1·13. It is very hard, and of a light or dark brownish-red colour, and contains, according to Jean (*Bull. Soc. Chim.* xxviii. 6), 15·7 per cent. of a tannic acid not identical with that of oak-bark or chestnut wood, and 2·8 per cent. of another astringent acid, which behaves with reagents like gallic acid, and is not fixed by animal skins. Arnaudon has found in it a colouring matter which gives a fine yellow dye. The watery decoction of the wood is slightly acid. Quebracho is as suitable as sumach

for the preparation of morocco leather, especially in the production of dark colours (*Dingl. pol. J.* cxxxi. 451).

On the gum of *Quebracho colorado*, see GUM (p. 916).

QUERCETAGETIN, $C^{27}H^{22}O^{13}$. A yellow colouring matter extracted from the flowers of the common marigold (*Tagetes patula*). Its reactions in alcoholic solution are the same as those of quercetin, but it differs from the latter in crystalline form and solubility in alcohol. The crystals contain 4 mols. water, which they give off at 100° . If quercetin be regarded as $C^{27}H^{20}O^{12}$ (*infra*), quercitagetin will be quercetin + H^2O (Latour a. Magnier de la Source, *Bull. Soc. Chim.* [2], xxviii. 337).

QUERCETIN. See QUERCITRIN.

QUERCITOL, $C^6H^{12}O^5$. *Quercite*.—This saccharine substance, obtained from acorns, was discovered in 1849 by Braconnot, who found that it does not ferment in contact with yeast. Dessaignes, in 1851, determined its composition, and showed that it is isomeric with mannitan and dulcitan, that is to say, that it contains the elements of mannitol, $C^6H^{14}O^6$, minus H^2O . Berthelot in 1855 showed that it is a polyatomic alcohol, and described several of its compound ethers. The results of all these investigations have already been described (v. 6).

A more complete examination of quercitol has lately been made by Prunier (*Ann. Chim. Phys.* 1878, [5], xv. 5-91), who has especially investigated the derivatives obtained from it by the action of the haloid acids and of acetic and butyric acid.

Prunier prepares quercitol by mixing the cold concentrated infusion of acorns with basic lead acetate, which throws down most of the impurities and colouring matter. The liquid is then fermented with yeast, freed from lead by means of sulphuric or carbonic acid and hydrogen sulphide, and evaporated. The white crystals thus obtained are finally purified by recrystallisation from dilute hydrochloric acid.

Quercitol crystallises in monoclinic prisms exhibiting, according to Sénarmont (*Jahresb. f. Chem.* 1857, 505), the combination $\infty P. \infty P \infty. 0P. + P. P \infty$, having the axial ratio $a : b : c = 0.8001 : 1 : 0.7662$, and the angle $ac = 68^\circ 57'$. Angle $\infty P : \infty P$ in the clinodiagonal principal section = $106^\circ 30'$; $P \infty : P \infty$ in the same = $108^\circ 52'$; $0P : +P \infty = 126^\circ 17'$; $0P : \infty P = 106^\circ 44'$.

Quercitol is optically dextrogyrate; $[\alpha]_D = 24.17^\circ$; has a density of 1.5845 at 13° ; dissolves in about 11 pts. of water at 12° , and in about 9 pts. at 20° ; is insoluble in alcohol, ether, benzene, and chloroform; melts at 225° . When heated at 100° for some days, quercitol gradually loses water and approximates to the composition $4C^6H^{12}O^5 - H^2O$. When heated to 240° in a vacuum it yields about three-fourths of its weight of an anhydride, $C^{12}H^{22}O^9 = 2C^6H^{12}O^5 - H^2O = (C^6H^{10}O^4)(C^6H^{12}O^5)$. This anhydride (which may be regarded as a compound of quercitol and quercitan) melts at 228° – 230° , dissolves much less freely than quercitol in water, and is nearly insoluble in alcohol and ether. Between 250° and 275° quercitol loses more water, and yields a sublimate of white, highly refracting, tabular crystals melting at 101° – 102° , the nature of which has not yet been determined. At 280° – 290° a totally different reaction takes place: the fused mass swells up enormously, giving off hydrogen, and the retort becomes filled with yellowish-green vapours of quinhydrone and quinol (hydroquinone), the latter of which condenses in long yellowish needles melting at 160° . This reaction may perhaps be explained as follows: a molecule of quercitol losing 3 mols. of water is first converted into quinol, $C^6H^{12}O^5 - 3H^2O = C^6H^6O^2$; and the quinol by loss of H^2 gives rise to quinone, which combines with more quinol to form quinhydrone, $C^6H^4O^2, C^6H^6O^2$.

Quercitol, when fused with potash, evolves hydrogen and yields quinol and quinhydrone, together with pyrogallol (or an isomeric substance), and oxalic and malonic acids.

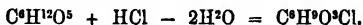
Acetoquercitols.—*Monacetoquercitol*, $C^6H^{11}(C^2H^3O)O^5$, formed on heating quercitol at 100° with glacial acetic acid in sealed tubes, is a white solid substance, difficult to crystallise. *Triacetoquercitol*, $C^6H^8(C^2H^3O)^3O^5$, is readily formed on heating quercitol at 130° – 140° with excess of glacial acetic acid containing 1 or 2 per cent. of acetic anhydride. It is a colourless amorphous solid, of bitter taste and faint aromatic odour, insoluble in water, soluble in alcohol and ether. *Pentacetoquercitol*, $C^6H^5(C^2H^3O)^5O^5$, is obtained by heating quercitol at 150° for many hours with excess of acetic anhydride. It is a colourless amorphous solid body, of very bitter taste, soluble in alcohol and ether, and very sparingly in water. The acetoquercites are more volatile than quercitol. When submitted to dry distillation they appear to yield *monacetoquercitan*.

Butyroquercitols.—*Monobutyroquercitol*, $C^6H^{11}(C^4H^7O)O^5$, formed on heating quercitol at 100° – 115° with butyric acid, is a semi-solid colourless body, of bitter taste, soluble in ether and less freely in alcohol and water. *Tributyroquercitol*,

$C^6H^7(C^4H^7O)^3O^4$, is formed on heating quercitol at 150° – 160° for many hours with excess of butyric acid. It is a syrupy uncrystallisable body, soluble in alcohol and ether. *Pentabutyroquercitol*, $C^6H^7(C^4H^7O)^5O^5$, is produced on heating the preceding compounds at 180° with a large excess of butyric acid. It forms a syrupy liquid of bitter taste, soluble in alcohol and ether, but scarcely so in water.

Quercitolchlorhydrins.—Quercitol treated with dilute hydrochloric acid, even at 100° , is simply dissolved in large quantity; but the concentrated acid attacks it in such a manner as to substitute HCl for the elements of water, whilst the strongest acid (saturated at 0°) exerts at the same time a dehydrating action, resulting in the formation of quercitan and its chlorhydro-derivatives.

Quercitol-monochlorhydrin, $C^6H^{11}ClO^4$, is formed on heating quercitol in the water-bath with excess of hydrochloric acid saturated at 10° . It is a white crystalline substance, soluble in ether and in alcohol, and melting at 198° – 200° . The mother-liquor contains *quercitan-monochlorhydrin*, $C^6H^9ClO^3$, a viscid uncrystallisable body soluble in absolute alcohol. *Quercitol-trichlorhydrin*, $C^6H^7Cl^3O^2$, formed on heating quercitol at 120° – 140° with excess of hydrochloric acid, crystallises in long flattened needles melting at 155° . *Quercitol-pentachlorhydrin*, $C^6H^5Cl^5$, obtained by heating the last compound afresh with hydrochloric acid, crystallises in slender yellow needles, fusible at about 102° . The mother-liquor contains quercitan-chlorhydrin, which is, indeed, the chief product, corresponding in quantity with two-thirds of the quercitol employed:



Quercitan, $C^6H^{10}O^4$, is obtained by saponifying with baryta the chlorhydrin just mentioned, neutralising exactly with sulphuric acid, and evaporating. It is a colourless uncrystallisable and slightly deliquescent substance, soluble in water and in alcohol, insoluble in ether. When dissolved in 85 per cent. spirit it gradually takes up water, becoming converted into quercitol.

Action of Hydrobromic Acid on Quercitol.—Hydrobromic acid (sp. gr. 1.7) appears to act on quercitol at 100° in the same manner as hydrochloric acid, producing a white crystalline substance soluble in water, and having the composition of *quercitol-monobromhydrin*. But at higher temperatures the action is entirely different, the products being aromatic bodies, including benzene, phenol, quinol, quinhedrone, quinone, and brominated derivatives of these last, which are still under examination.

Action of Hydriodic Acid on Quercitol.—Quercitol when distilled with hydriodic acid saturated at 0° , yields benzene (in quantity corresponding with half the quercitol employed), phenol, iodophenol, quinone, quinol, hydroxyquinones, and volatile iodised products transformable into C^6H^{14} . The cold acid dissolves quercite freely, with slight rise of temperature, but no hydriodide has been isolated.

In accordance with the foregoing results, quercitol may be regarded as belonging either to the fatty or to the aromatic series of compounds. On the one hand, its behaviour with acids shows that it is a polyatomic alcohol capable of yielding a series of ethers of the general formula $C^6H^2(H^2O)^n + nA - nH^2O$, in which A represents a monobasic acid and $n = 1, 3$, or 5 . Its decomposition by heat and by the action of potash, or of hydrobromic or hydriodic acid, indicates, on the other hand, its derivation from benzene: $C^6H^6 - 2H^2 + 2H^2O = C^6H^8O^2$ (quinol); and $C^6H^8O^2 + 3H^2O = C^6H^{12}O^5$ (quercitol). It is the type of a group of bodies forming a connecting link between the two series.

QUERCITRIN and QUERCETIN (J. Löwe, *Zeitschr. anal. Chem.* 233, 247). Quercitrin is usually regarded as a glucoside, since, according to the statements of various chemists (v. 4, 6), it is resolved, on boiling with dilute acids, into sugar and quercetin. Löwe, however, finds that quercitrin is not a glucoside, inasmuch as it differs from quercetin only by a certain number of molecules of water, and may be, for the most part, converted into the latter substance by simply heating its aqueous solution, in which change no sugar is produced.

To prepare quercitrin, Löwe exhausts with alcohol the quercitron-bark of commerce, evaporates the filtered extract, dissolves the residue in water, and shakes the solution repeatedly with ether. The residue left on evaporating the ethereal liquid is taken up with alcohol, and mixed with a large quantity of hot water, to separate the quercitrin. The product, after recrystallisation from boiling water and prolonged drying over sulphuric acid, forms light yellow shining scales, and gives on analysis numbers agreeing with the formula $C^{15}H^{10}O^9$. The crystals lose water at 120° , melt at 130° – 133° without further loss, and solidify to a brownish-yellow mass on cooling. The fused substance gives on analysis numbers agreeing with the formula $C^{15}H^{14}O^8$. The above formula of quercitrin was confirmed by analyses of two lead-salts, which were found to have the formulæ $C^{15}H^{12}O^7 \cdot 2PbO$ and $C^{15}H^{14}O^8 \cdot PbO$.

Quercetin.—Quercitrin suspended in water and heated at 110° for some days in sealed tubes, is resolved for the most part into a body having the properties of quercetin and giving on analysis numbers agreeing with the formula $C^{18}H^{12}O^7$. Quercetin may therefore be regarded as an anhydride of quercitrin. This result accords with the fact previously known, that quercitrin yields quercetin by dry distillation.

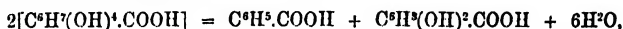
Löwe also finds that when an aqueous solution of catechu is shaken up with ether, the ether takes up quercetin, which may thus be shown to exist in all kinds of catechu, though in many varieties the proportion is so small that it can be detected only when several pounds of material are operated on. The existence of this substance, which in itself is almost insoluble in cold water, in a cold extract, is due, according to Löwe, to the presence of catechutannic acid. From sumach, especially the Sicilian variety, Löwe obtained yellow needles or flocks, moderately soluble in hot water, and exhibiting all the reactions of quercitrin.

QUINCE-MUCILAGE. See PLANT-MUCILAGE (p. 1638).

QUINHYDRONE. See QUINONE (p. 1741).

QUINIC ACID, $C^8H^{12}O^8 = C^6H^7(OH)^4.COOH$. Ethyl quinate, treated with acetic anhydride, is converted into ethylic tetracetylquinate, $C^8H^{17}(OC^2H^3O)^4.COOC^2H^3$, showing that quinic acid contains four hydroxyl-groups. Ethylic tetracetylquinate is almost insoluble in cold, and only sparingly soluble in boiling water, but dissolves easily in hot alcohol and ether. It crystallises from boiling water in plates (m. p. 135°), and can be sublimed without decomposition. By slow evaporation of the ethereal solution, it can be obtained in large colourless rhombic crystals.

Quinic acid, heated with hydrobromic acid in sealed tubes at 130° , yields benzoic and protocatechuic acids, thus:



together with small quantities of parabromophenol and quinol. These facts show that quinic acid is nearly related to hexhydrobenzene and quercite, thus:—

C^6H^{12}
Hexhydrobenzene.

$C^6H^7(OH)^5$
Quercite.

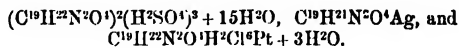
$C^6H^7(OH)^4.COOH$
Quinic acid.

(Fittig a. Hillebrand, *Liebigs Annalen*, xciii. 194).

According to O. Loew (*J. pr. Chem.* [2], xix. 309), quinic acid is a constituent of hay, and the hippuric acid which is present in the urine of herbivorous animals is perhaps one of its products of decomposition.

QUININE, QUINIDINE, and ALLIED BASES. See CINCCHONA-BASES (pp. 489–495).

Oxidation-products of Quinine.—When a solution of quinine sulphate, which has been acidified with sulphuric acid, is oxidised in the cold by potassium permanganate, it splits up into formic acid and *quitenine* or *chitenine*, $C^{19}H^{22}N^2O^4 + 4H^2O$, according to the equation $C^{20}H^{24}N^2O^2 + 2O^2 = C^{19}H^{22}N^2O^4 + CH^2O^2$. Quitenine, which is identical with Kerner's *α-dihydroxyl-quinine* (*Zeitschr. f. Chem.* 1869, 593), is separated from the precipitated manganese dioxide by repeated lixiviation with boiling alcohol. It crystallises in colourless prisms, which are insoluble in ether and in absolute alcohol, but dissolve freely in acids, and in water to which a few drops of ammonia or potash have been added. Quitenine is a weak base, and forms the following compounds:



Quininic acid, $C^{11}H^8NO^3$, is obtained by oxidising quinine with chromic acid, neutralising the product with baryta-water, and decomposing the barium salt with hydrochloric acid. On evaporating the solution, quininic acid separates in prisms. The mother-liquor is treated with lead carbonate, and the lead salt decomposed by sulphuretted hydrogen. A non-crystalline syrupy liquid is thus obtained, which resembles the crystalline acid in its chemical properties (Skraup, *Ber.* xii. 1104).

Periodides of Quinine and Allied Bases. The *sulphato-periodides* of these bases have already been described (pp. 479, 486, 489–491, 493). The following acid periodides have also been described by Jörgensen (*J. pr. Chem.* [2], xv. 65, 418).

Selenato-periodides.—These salts are formed by treating the selenates of alkaloids with a mixture of alcoholic iodine-solution and hydriodic acid. *Selenic Herapathite*, $4C^{20}H^{21}N^2O^2.3H^2SeO^4$, obtained by mixing the calculated quantities of its constituents in hot alcoholic solution, is isomorphous with ordinary herapathite and closely resembles it, but is less soluble; it does not dissolve in carbon sulphide, ether,

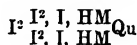
or chloroform. The alcoholic solution when shaken up with mercury yields not a trace of mercurous iodide, but a colourless iodine double salt, strongly resembling the corresponding sulphur-compound. Treated in alcoholic solution with tincture of iodine, it yields bronze-yellow needles, probably analogous to the third quinine sulphato-periodide (p. 490), and on dissolving these crystals in hot alcohol, an olive-grey compound separates, resembling the second sulphato-periodide of quinine.

Selenato-periodides of Quinidine.—(1). $2C^{20}H^{24}N^2O^4 \cdot H^2SeO^4 \cdot 2HI, I^4$, prepared with deficient iodine, but with calculated quantities of the other constituents, crystallises in red-brown orthorhombic prisms, resembling the corresponding sulphur-compound. Optical action * || comparatively light; + comparatively dark brown. When shaken in alcoholic solution with mercury, it yields an iodine double salt which does not melt when heated with an insufficient quantity of iodine, like that formed from the sulphate.

(2). $4C^{20}H^{24}N^2O^4 \cdot 4I^2 \cdot SeO^4 \cdot 3HI, I^6$, is prepared like the second sulphato-periodide of quinine (p. 490), which it very much resembles, excepting that it is somewhat darker. Polarisation strong; || opaque; + olive-yellow. Shaken with mercury, it forms an iodine double salt, which melts when heated, and resolidifies amorphous. The formula of this selenato-periodide is probably: †



a view which is supported by the fact that its alcoholic solution, when agitated, yields crystals of the compound:



Selenato-periodide of Cinchonine, $2C^{20}H^{24}N^2O^4 \cdot H^2SeO^4 \cdot 2HI, I^4$, is prepared like the third sulphato-periodide (p. 479), which it closely resembles.

Selenato-periodides of Cinchonidine: (1). $C^{20}H^{24}N^2O^4 \cdot 9H^2SeO^4 \cdot 8HI, I^{24} + 8H^2O$, is prepared like the sulphur-compound (p. 486), which it closely resembles; it must be washed with strong alcohol. Optical character: || opaque; + very faint olive-green.

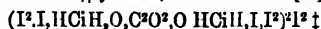
(2). $2C^{20}H^{24}N^2O^4 \cdot H^2SeO^4 \cdot III, I^4 + H^2O$, formed, with separation of H^2SeO^4 and III , by the action of dilute alcohol on the last compound. When recrystallised from dilute alcohol, it forms red-brown needles resembling the fourth sulphato-periodide (p. 486).

Phosphato-periodide of Cinchonidine, $2C^{20}H^{24}N^2O^4 \cdot 2PH^3O^4 \cdot HI, I^4$, separates from an alcoholic solution of calculated quantities of its constituents, in long dark-brown shining needles which have a bluish reflex and polarise slightly: || lighter, + darker brown. It contains unaltered cinchonidine. The hot alcoholic solution, shaken up with mercury, yields mercurous iodide and a double salt. There is also at least one more phosphato-periodide of cinchonidine, obtained under circumstances not definitely known, in dark brown laminæ with violet reflex, probably having the composition $4C^{20}H^{24}N^2O^4 \cdot 3PH^3O^4 \cdot 4HI, I^{12}$.

Arsenato-periodide of Cinchonine, $2C^{20}H^{24}N^2O^4 \cdot 2AsH^3O^4 \cdot HI, I^4$, exactly resembles the corresponding phosphate.

Oxalato-periodide of Cinchinine, $4C^{20}H^{24}N^2O^4 \cdot 2C^2H^2O^4 \cdot 4HI, I^{10}$, is formed when 1 mol. cinchonine, dissolved in 20 c.c. normal oxalic acid and alcohol, is mixed with 1 mol. HI and 3 at. I , and separates in the purest state from dilute solutions; it forms black, shining, apparently orthorhombic prisms, mostly quite opaque. When shaken up with mercury, it yields indistinct yellow granules of a double salt, together with mercurous iodide.

Oxalato-periodide of Cinchonidine, $2C^{20}H^{24}N^2O^4 \cdot C^2H^2O^4 \cdot 2HI, I^4$, separates from the hot alcoholic solution of calculated quantities of its constituents in thin red-brown needles. Polarisation || yellow; + brown to opaque. Rational formula:



When agitated with mercury, it yields no mercurous iodide, but only a double salt in slender pale yellow needles.

Oxalato-periodides of Methylquinine.—Several of these salts appear to be producible, but they are all very much alike in physical properties and solubility; two which crystallise in black prisms appear to be represented by the formulæ $2C^{20}H^{24}N^2O^4 \cdot CH^3I, 2C^2H^2O^4 \cdot I^3$ and $2C^{20}H^{24}N^2O^4 \cdot CH^3I, 2C^2H^2O^4 \cdot I^4$.

* || with parallel Nicols; + with crossed Nicols.

† $M = C^{20}H^{24}N^2O^4 \cdot HI, SeO^4$; $Qu = C^{20}H^{24}N^2O^4$.

‡ $Cl = C^{20}H^{24}N^2O^4$.

Tartrato-periodide of Cinchonidine, $2C^{20}H^{14}N^2O, C^4H^4O^4, HI, I^2$, is formed when 1 mol. cinchonidine is dissolved with at least 2 mol. tartaric acid, and 1 mol. HI in 100 c.c. strong alcohol, and the solution is mixed with 1 at. iodine. It forms long thin red-brown prisms which, when shaken with mercury, yield no mercurous iodide, but an oily, yellow, gummy double salt.

Hydrochloro periodides of Quinine: (1). $3C^{20}H^{14}N^2O^2, 8HCl, 4HI, I^2$, crystallises in blackish-green flat needles when pure quinine (1 mol.) is heated with a large excess of dilute hydrochloric acid and alcohol, and an alcoholic solution of 2 mols. iodine is then added. The crystals polarise strongly: || brown to brownish-yellow; + opaque. By agitating it with mercury, a large quantity of mercurous iodide is formed, together with an amorphous double salt. (2). $4C^{20}H^{14}N^2O^2, 8HCl, 5HI, I^2$, is formed in light brown crystals when 1 mol. quinine is brought in contact with 3 mols. hydrochloric acid, and 3 mols. potassium iodide in solution; it must be quickly filtered off and dried. The polarising power of this salt is very feeble. When dry, it requires a temperature above 100° to melt it, but under boiling water it melts easily with separation of iodine.

Hydrochloro-periodide of Cinchonine, obtained like the quinine-compound, crystallises in long brown shining prisms, and when shaken with mercury, yields no iodide, but only a pale-yellow, oily, mercury double salt.

Jørgensen considers that the iodine in all these compounds is present in two different forms, viz., as hydrogen iodide, and in a looser form of combination, in which it may be called 'molecular iodine,' since it exhibits many of the properties of free iodine, acting, for example, on polarised light like the tourmaline, a property which Jørgensen has shown to be possessed by crystallised iodine.

QUINIRETIN. This name is given by Flückiger (*Pharm. J. Trans.* [3], viii. 885) to a substance, probably isomeric with quinine, which is produced by the action of light on quinine in solution. A clear solution of 1 pt. quinine in 2000 pts. water, exposed to summer sunshine, assumed a yellowish or brownish coloration, and after a few days deposited a flocculent brown precipitate, only a very small trace of alkaloid being left in solution. This change takes place when quinine dissolved in water previously freed from air by boiling is exposed to sunlight, also on exposing a solution of quinine to the direct rays of the sun in an atmosphere of hydrogen. Quiniretin has no alkaline reaction, neither does it neutralise acids, in which, however, it is freely soluble; it has a very bitter taste, and is insoluble in alcohol, ether, and water. The hydrochloric acid solution is precipitated by ammonia, but not by tannin. Nessler's solution produces a precipitate. It is dissolved by chlorine-water, the solution yielding a green precipitate when treated with ammonia. Quinine in the dry state is not so readily transformed as when it is dissolved in water or alcohol. The other cinchona alkaloids, being more sparingly soluble in water, are not so easily changed. Solutions of quinic acid, concentrated or dilute, are scarcely affected by exposure. Aqueous solutions of morphine or strychnine are only slightly coloured, whilst codeine or brucine are coloured very strongly. The solubility of the alkaloid seems to play a prominent part in the transformation, but the subject requires further investigation.

QUINIZARIN, $C^{14}H^{10}O^4 = C^6H^4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C^6H^2(OH)^2$ (Liebermann a. Giesel, *Ber.*

x. 606). This isomeric of alizarin, which Grimm obtained by heating quinol with sulphuric acid and phthalic anhydride (p. 102), is likewise produced when a mixture of phthalic anhydride and parachlorophenol, in equal numbers of molecules, is heated for some hours at 110° with a quantity of sulphuric acid equal to ten times the weight of the chlorophenol. In this way 8 to 10 per cent. of the chlorophenol is converted into quinizarin. A certain quantity of purpurin is formed at the same time, but can be easily separated, as quinizarin is almost insoluble in a cold solution of sodium carbonate.

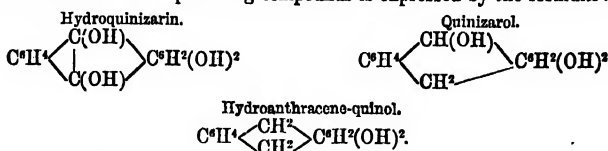
Reduction-products.—Quinizarin, boiled with dilute hydriodic acid and phosphorus, or heated with hydrochloric acid and stannous chloride, is reduced to hydroquinizarin, $C^{14}H^{10}O^4$, which crystallises from alcohol in yellow needles. It forms an insoluble yellow barium salt, and its alkaline, yellow, fluorescent solution readily absorbs oxygen, and is reconverted into quinizarin. Sometimes if the reaction is carried on longer it goes further, producing quinizarol, $C^{14}H^{12}O^3$, which resembles hydroquinizarin.

When quinizarin is boiled for an hour with hydriodic acid of sp. gr. 1.8, and an excess of phosphorus, it yields hydroanthracene-quinol, $C^{14}H^{12}O^2$, which is readily soluble in alcohol, ether, and acetic acid, and crystallises in yellowish-white rhombic plates melting at 99° ; its solutions show a strong greenish-yellow fluorescence; it volatilises with steam; the alcoholic solution is coloured green by ferric chloride. It forms a crystalline potassium salt, $C^{14}H^{11}O^2K$, and insoluble yellow lead and copper

salts, which are obtained by precipitating the alcoholic solution containing a little ammonia with the corresponding acetates, the lead compound, $(C^{14}H^{10}O^2)_2Pb$, forming microscopic needles. On heating the quinol with a mixture of acetyl chloride and acetic anhydride, the compound $C^{14}H^{11}O^2.C^2H^2O$ is obtained, forming pale yellow warty crystals, which melt at 136° – 138° .

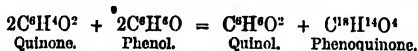
An ammonia compound could not be obtained, but ethylamine acts readily on the quinol, yielding the compound $C^{14}H^{10} \begin{smallmatrix} OH \\ \diagup \diagdown \\ NH(C^2H^5) \end{smallmatrix}$, which crystallises in lemon-yellow silky needles, melting at 162° and decomposed by boiling alkalis. When the quinol is boiled with acetic acid, manganese dioxide, and sulphuric acid, it is oxidised to $C^{14}H^8O^2$, which crystallises in orange-coloured needles melting at 191° .

The constitution of the preceding compounds is expressed by the formulæ:



QUINOL, $C^8H^6O^2 = C^6(OH).H.H.OH.H.H$. *Paradihydroxybenzene* (hitherto called *Hydroquinone*: see NOMENCLATURE, p. 1420).

Formation and Preparation.—1. Together with phenoquinone (vii. 1036) by adding quinone to a solution of phenol, the phenoquinone dissolving while the quinol separates out:



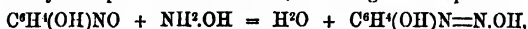
(Wichelhaus, *Ber.* v. 248).

2. By boiling an aqueous solution of diazophenol sulphate with 10–15 per cent. strong sulphuric acid:



The quinol may be extracted from the product by ether after cooling. The yield amounts to 46·2 per cent. If no sulphuric acid is added, resinsation takes place on boiling. Strong hydrochloric acid may also be added instead of sulphuric acid, in which case from 30 to 36 per cent. quinol is obtained, together with resin (Weselsky a. Schuler, *Ber.* ix. 1159).

3. By the action of hydroxylamine hydrochloride on a dilute aqueous solution of nitrosophenol. No action takes place in the cold, but on gently heating the liquid, torrents of nitrogen are given off, and the solution is found to contain quinol. Probably diazophenol is first formed, according to the equation:



and then converted into quinol in the manner above explained (E. Hepp, *Ber.* x. 1654).

4. By reducing the methylic ether of paranitrophenol with tin and hydrochloric acid, converting the resulting paranitranisidine by the action of nitrous acid into paradiazo-anisole, and decomposing the sulphate of this base with water. The salts of paradiazo-anisole are but slowly decomposed by boiling with water or dilute acids, and it is therefore better to heat the solution for some hours in a sealed tube at about 140° . The greater part of the diazo-compound is thereby converted into a brown viscid substance, probably consisting for the most part of methyl-quinol, while a small portion is converted into quinol, which may be extracted from the watery liquid in the tube by agitation with ether (H. Salkowski, *Ber.* vii. 1008).

5. From bromosalicylic acid, $C^6.OH.CO^2H.H.Br.H.H$ (which, when heated, yields [1 : 4] bromophenol), by fusion with sodium hydroxide, whereby it is converted into the corresponding hydroxysalicylic acid, $[OH : CO^2H : OH = 1 : 2 : 4]$, m. p. 196° – 197° , and heating this latter in a sulphuric acid bath at 215° , whereupon pure quinol sublimes; if the acid be distilled from a retort over an open flame, catechol (pyrocatechin) will pass over, though in subordinate quantity, together with the quinol (Rakowski a. Leppert, *Ber.* viii. 788).

6. Together with quinone and other products by heating quercitol above 280° (p. 1740).

7. By passing a current of air for three or four hours through an alkaline solution of ethyl succinosuccinate (see SUCCINIC ETHERS), mixing the resulting brown liquid with excess of acetic acid, filtering, and treating the filtrate with sulphuric acid, which throws down a yellow crystalline body, containing, together with other products,

quinol-dicarboxylic acid, $C^6H^4O^2(COOH)^2$, which, when heated with potassium hydroxide, yields quinol (F. Herrmann, *Ber.* x. 107).

8. Quinol may be prepared from aniline by the following process. 1 pt. of aniline is dissolved in 8 pts. of sulphuric acid diluted with twice its bulk of water, and to this solution, after cooling, a saturated solution of $2\frac{1}{2}$ pts. of potassium bichromate is added gradually, too great a rise of temperature being avoided. The thick pulpy mass of aniline-black produced at first changes after a time to a dirty-brown solution, which is then to be treated with sulphur dioxide in excess, and afterwards agitated with ether. The ethereal liquid, when distilled, leaves a brownish crystalline residue of crude quinol, amounting to 16 per cent. of the aniline employed.

Toluquinol may be prepared in the same manner from orthotoluidine (Nietzki *Ber.* x. 1934).

Crystalline Form.—According to O. Lehmann (*Zeitschr. f. Kryst.* i. 44), quinol is dimorphous, one of its modifications being the ordinary stable form which the compound assumes when crystallised from water, the other the unstable form produced on sublimation. This latter takes the form of laminar monoclinic crystals, in which $a : b : c = 2.605 : 1 : 1.558$ and $ac = 73^\circ$. The measurements (only approximate) give the faces $OP, \infty P, +P$, and the angle $+P : -P = 112^\circ 4'$. The plane of the optic axes is the plane of symmetry. On a plate inclined to the median line, the angle of the optic axes in oil is 92° . The stable modification is hexagonal (rhombohedral-hemihedral). Axes $a : c = 1 : 0.6591$. The crystals are elongated prisms of the second order, with the face $\infty P2$, at the end of which there occurs only $+R$ or $-R$, as well as $-R$. The observed angles are $-R : -R = 62^\circ 57'$; $+R : \infty P2 = 58^\circ 22'$. Double refraction slightly positive. The crystals of the unstable modification appear to change into the stable modification when left to cool slowly after their formation.

Melting Point.—Hlasiwetz u. Habermann (*Ber.* viii. 684) find, in opposition to all previous statements, that the true melting point of quinol is 169° —a result which establishes its identity with pyrogentisic acid, the product obtained by the action of heat on gentisic acid (p. 860).

Reaction with Nitrous acid.—When nitrous gas is passed into a solution of quinol (in ether?), cooled with ice as long as it continues to be absorbed, small golden-yellow needles separate, probably consisting of dinitrodihydroxyquinone, $C^6(NO^2)_2O^2(OH)^2$, the quantity increasing on addition of water, and red fumes being at the same time evolved (Nietzki, *Ber.* x. 2147).

Derivatives of Methyl- and Ethyl-quinols. *Dichlorodimethylquinol*, $C^6H^2Cl^2(OCH^3)^2$, separates in colourless needle-shaped crystals when chlorine-gas is passed into a solution of dimethyl-quinol in glacial acetic acid. It melts at 126° , dissolves in ether, alcohol, and hot glacial acetic acid, but is insoluble in water. *Tetrachlorodimethylquinol*, $C^6Cl^4(OCH^3)^2$, is formed on saturating the mother-liquor of the dichloro-compound with chlorine, and separates in yellowish-white needles which melt at 153° – 154° , but begin to sublime at a lower temperature. It dissolves easily in alcohol and ether. The filtrate from the tetrachloroquinol contains tetrachloroquinone and another chloro-compound, which is very soluble in alcohol, and sublimates in violet crystals melting at 79° (Habermann, *Ber.* xi. 1034).

Dibromodimethylquinol, prepared by slowly adding bromine to a solution of dimethylquinol in hot glacial acetic acid, forms colourless crystals, which melt at 142° , and sublime without decomposition. It is soluble in boiling glacial acetic acid, and insoluble in water (Habermann).

Nitrodimethylquinol, $C^6H^2(NO^2)(OCH^3)^2$, separates in golden-yellow crystals, when strong nitric acid is added to an emulsion of dimethylquinol and warm water; it melts at 70° – 71° , sublimates at higher temperatures, and dissolves in alcohol.

Dinitrodimethylquinol is obtained by mixing a solution of dimethylquinol in glacial acetic acid with an equal volume of strong nitric acid, leaving the mixture at rest for a quarter of an hour, and then adding water, which precipitates the nitro-compound in the form of a yellow crystalline powder. It is soluble in alcohol and glacial acetic acid, but insoluble in water; melts at 169° – 170° , and sublimates readily.

Trinitrodimethylquinol is formed on adding a solution of dimethylquinol or of dinitrodimethylquinol in glacial acetic acid, to a well-cooled mixture of sulphuric and fuming nitric acids. On dilution with water, a yellow precipitate is produced, which dissolves in hot alcohol, and is deposited from the alcoholic solution in yellow brittle prisms (Habermann).

Nitrodiethylquinols (Nietzki, *Ber.* xi. 1448; xii. 38).—The *mononitro-compound*, $C^6H^4(NO^2)(OC^2H^5)^2$, prepared by mixing a solution of diethylquinol in 5 pts. glacial acetic acid with an equal volume of nitric acid sp. gr. 1.25, crystallises from

an alcoholic solution in golden-yellow needles melting at 49° . By the further action of nitric acid, it is converted into two *dinitro-derivatives*, $C^6H^2(NO^2)^2(OC^2H^3)^2$, one melting at 176° , the other melting at 130° , and dissolving freely in alcohol (Nietzki, *Ber.* xii. 38). The first of these compounds is also formed, together with a trinitro-derivative, by adding a solution of diethylquinol in acetic acid to fuming nitric acid, and without admixture of the trinitro-compound, by treating diethylquinol with weaker nitric acid. As thus obtained, it forms lemon-yellow laminae, insoluble in water, easily soluble in alcohol, melting at 172° .

Trinitrodiethylquinol, $C^6H(NO^2)^3(OC^2H^3)^2$, obtained by the action of a mixture of nitric and sulphuric acids on diethylquinol, crystallises from alcohol in long pale straw-yellow needles melting at 133° , and turning orange-yellow when exposed to light. Heated in sealed tubes with alcoholic ammonia, it is converted into a red compound, $C^6H^2N^2O^3$, or probably $C^6H(NO^2)^2(NH^2)^2(OC^2H^3)$, formed by replacement of the ethoxyl-group by NH^2 , and of the nitro-group by another NH^2 -group. This compound is neither acid nor basic; but when boiled with potash it gives off ammonia, and is converted into a bibasic acid, $C^6H^2N^2O^7$, or $C^6H(NO^2)^2(OH)^2(OC^2H^3)$, which crystallises from alcohol in golden-yellow needles having a violet reflex, melts with decomposition at 143° , dissolves sparingly in water, easily in alcohol, ammonia, and alkalis. Its alkali-salts are easily soluble; the barium salt forms sparingly soluble orange-coloured needles.

Diamidodiethylquinol, obtained by the action of tin and hydrochloric acid on the dinitro compound, is converted by nitrous acid into a body having the composition $C^{10}H^2N^2O^2$; thus: $C^{10}H^{12}(NH^2)^2O^2 + N^2O^2H = 2H^2O + C^{10}H^{12}N^2O^2$. This compound crystallises in colourless needles, melts at 233° , dissolves in absolute alcohol and glacial acetic acid; also in caustic alkalis, and is precipitated therefrom by acids (Nietzki).

Azo-diethylquinol, $C^{10}H^{12}N^2O^4 = (C^2H^3O)^2C^6H^2-N=N-C^6H^2(OC^2H^3)^2$, is formed, together with a hydrazo-derivative, by treating a solution of mononitrodiethylquinol in alcoholic potash with a small quantity of zinc-dust. The liquid, which at first assumes a deep-red colour, is decolorised by prolonged boiling with zinc-dust, but quickly recovers its red colour on exposure to the air; and on pouring the decolorised solution into water, a crystalline product separates, which appears, on examination with the microscope, to be a mixture of two bodies, viz. colourless needles of the hydrazo- and deep red laminae of the azo-compound. These two bodies cannot be separated by fractional crystallisation, on account of the ready oxidisability of the hydrazo-compound; but on washing the mixture with water to remove potash, and then warming it with dilute hydrochloric acid, the hydrazo-compound passes completely into solution, while the azo-compound remains behind, and may be purified by recrystallisation from alcohol. It crystallises in red plates, dissolves in ether, benzene, and hot alcohol—also in strong hydrochloric and sulphuric acids, forming violet solutions from which it is precipitated by water. It melts at 128° , and distils at a higher temperature (Nietzki, *Ber.* xii. 38).

Hydrazotetretethylquinol, $C^{20}H^{28}N^2O^4 = (C^2H^3O)^2C^6H^2.NH.NH.C^6H^2(OC^2H^3)^2$, as already observed, is extremely oxidisable, and has not been obtained in the pure state; but the base, $NH^2.C^6H^2(C^2H^3O)^2.C^6H^2(C^2H^3O)^2.NH^2$, related to it in the same manner as benzidine to hydrazobenzene, is obtained as hydrochloride by concentrating the acid solution filtered from the azo-compound above mentioned. The hydrochloride, $C^{20}H^{28}N^2O^4.2HCl$, then crystallises, especially in presence of an excess of hydrochloric acid, in long slender needles. This salt is but slightly soluble in water, even when hot, and nearly insoluble in moderately strong hydrochloric acid, and on adding hydrochloric acid to its warm saturated solution, every drop produces a gelatinous precipitate; this reaction affords an easy mode of purifying the salt. The aqueous solution of the hydrochloride forms with *platinic chloride* a yellow crystalline precipitate of the platinum salt, $C^{20}H^{28}N^2O^4.2HCl, PtCl_4$.

The base separated from the hydrochloride by alkalis crystallises from alcohol in delicate colourless laminae, resembling benzidine, and melting at 129° (corr.) Its aqueous solution, when treated with oxidising agents, becomes dark brown and deposits a brownish iridescent precipitate (Nietzki, *Ber.* xii. 40).

QUINOL-CARBOXYLIC ACID. This name is given to the hydroxysalicylic acid, $C^6.OH.CO^2H.H.OH.H^2$ (m. p. 196° – 197°), obtained by fusing the bromosalicylic acid of corresponding constitution with potassium or sodium hydroxide (p. 289). The acid of the same composition, obtained in like manner from the corresponding iodosalicylic acid, melts at the same temperature, and likewise yields quinol when heated in a sulphuric acid bath at 215° , but appears to differ somewhat in its relations to solvents from the acid obtained from the bromosalicylic acid. When quinolcarb-

oxylic acid in aqueous solution is treated with weak oxidising agents, a product is formed, from which ether extracts a crystallisable acid [quinone-carboxylic acid?], which is instantly decolorised by reducing agents. The acid named by Hesse *carbohydroquinonic acid* (iii. 214), yields, when heated, as observed by Lautemann (iii. 215), not quinol, but catechol (Rakowski a. Leppert, *Ber.* viii. 788, 976).

Quinol-dicarboxylic acid, $C^6H^4O_2(COOH)_2$, is formed, as already stated (p. 1738), by passing a current of air through a solution of ethylic succino-succinate containing an excess of alkali. When precipitated by sulphuric acid and purified by repeated crystallisation from boiling water, it forms tufts of long interlaced needles of light brownish-yellow colour, very soluble in alcohol and ether, sparingly in cold, abundantly in boiling water, the solutions having a light yellow colour, and exhibiting a faint greenish fluorescence; with ferric chloride they yield a pure deep blue colour. The acid is not fusible, and only a very small portion of it sublimes without decomposition. When cautiously fused with potassium hydroxide, it yields quinol (F. Herrmann, *Ber.* x. 107).

QUINOL ETHER. See QUINYL OXIDE.

QUINOL-PHTHALEIN. See PHTHALEINS (p. 1612).

QUINOLSULPHONIC ACID, $C^6H^4SO_3 = C^6H^4 \begin{smallmatrix} OH \\ \diagup \\ O.SO_3H \end{smallmatrix}$. The crystalline form of the potassium salt of this acid, $C^6H^4KSO_3$, has been determined by C. Bodewig (*Zeitschr. f. Kryst.* i. 584). It belongs to the orthorhombic system, $a : b : c = 0.7641 : 1 : 2.0965$. Observed forms $0P$, $\frac{1}{2}P$, P , \bar{P} , $\infty \bar{P} \infty$. The crystals are developed tabularly and irregularly in the direction of the basal face. The plane of the optic axes is parallel to $\infty \bar{P} \infty$. The axis c is the first median line. Double refraction positive. Apparent angles of the axes in oil:

Li-red
83° 16'

Na-yellow
83° 29'

Tl-green
84° 31'

QUINONE, $C^6H^4O_2 = C^6H^4 \begin{smallmatrix} O \\ \diagup \\ O \end{smallmatrix}$ [1 : 4]. This compound is formed by the oxidis-

ing action of manganese dioxide and sulphuric acid on paraphenolsulphonic acid [the meta-acid yields none], and on sulphanilic (*p*-amidobenzenesulphonic) acid (Schrader, *Ber.* viii. 759). According to Prunier (*Bull. Soc. Chim.* [2], xxv. 515; xxviii. 180), quinone occurs, together with quinol, amongst the products of decomposition of quercitol by heat (above 280°) and by hydriodic acid.

Preparation from Aniline.—Powdered potassium dichromate is added to a cold mixture of 1 pt. aniline, 8 of sulphuric acid, and 30 of water, until the precipitate of aniline black which is first formed redissolves, giving a brown solution. About $2\frac{1}{2}$ pts. of potassium dichromate are required for this purpose. If the process is now interrupted by the addition of a sulphite, quinol is obtained, but in order to prepare the quinone, it is necessary, after adding potassium dichromate (1 pt.), again to leave the mixture at rest for some hours, and then heat it to 35°. The quinone is extracted by agitation with ether, as by this means 68 per cent. of the theoretical yield of quinone is obtained, whilst the amount is comparatively small if the quinone is distilled off in the current of steam. Quinone separates from the ethereal solution in golden scales, which generally contain traces of quinhydrone. The mother-liquor from the quinone may be worked up for quinol (Nietzki, *Ber.* xi. 1102).

Detection.—A very delicate test for quinone in aqueous solution is afforded by an alcoholic solution of *hydrocærulignone*. On addition of a drop or two of this liquid, the quinone solution assumes at first a yellowish-red colour, but quickly becomes colourless again, and deposits steel-blue iridescent needles of *cærulignone* (p. 548). This reaction will detect 1 pt. of quinone in 200,000 pts. of water, and the orange coloration is still perceptible with 1 pt. quinone in 1,000,000 pts. of water. With *thymoquinone*, the reaction is either not produced at all or is very indistinct. On the other hand, *hydrocærulignone* may be used as a test for many other oxidising agents.

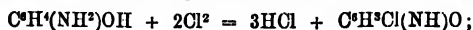
Tetrabromoquinone, $C^6Br^4O_2$, is formed by the action of bromine in excess on quinone dissolved in hot glacial acetic acid (Saraw, *Ber.* xii. 680).

Trichloroquinone is converted by aniline into *dianilidomonochloroquinone*, $C^{12}H^{12}N^2ClO_2$, which crystallises in plates having a metallic lustre (Neuhöffer a. Schultz, *Ber.* x. 1792).

Chlorimidoquinone, $C^6H^4ClNO = C^6H^4Cl \begin{smallmatrix} O \\ \diagup \\ NH \end{smallmatrix}$ [O : Cl : NH = 1 : 2 : 4]

(R. Schmitt a. Benewitz, *J. pr. Chem.* [2], viii. 1; R. Schmitt, *ibid.* xix. 312). This

compound, originally regarded as dichlorazophenol, is formed by the action of aqueous chloride of lime on paramidophenol hydrochloride, according to the equation :

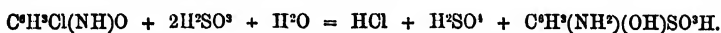


and in like manner from paramidophenetol, ethyl chloride being then given off as well as hydrogen chloride :



It is best prepared by dissolving 3 g. paramidophenol hydrochloride in 150 g. water, and dropping in from a burette, with agitation, a strong solution of bleaching powder. A point is then soon reached at which the chlorimidoquinone, which separates in white flocks, no longer redissolves, but increases on further addition of the chlorine-solution, the colour of the liquid at the same time becoming fainter and fainter, till at the moment of completion of the reaction, it suddenly changes from violet to yellow; the addition of the chlorine-solution must then be discontinued. The chlorimidoquinone is easily separated from the liquid by filtration, and may be freed from calcium chloride by washing with a little water, and dried over sulphuric acid, which process, however, is attended with some loss, on account of the volatility of the compound. It may also be purified, though likewise with some loss from decomposition, by distillation with steam.

Chlorimidoquinone is sparingly soluble in cold, easily in hot water, also in alcohol, benzene, ether, and glacial acetic acid, and crystallises from the last-mentioned solvent in tufts of yellow needles often several millimeters long. It melts at 86°, and decomposes with slight detonation when heated a few degrees higher. It smells very much like quinone, and further resembles the latter by the deep brown colour which it imparts to the hands and to organic substances in general. It is readily decomposed by potash-ley and strong sulphuric acid, with formation of brown humus-like substances. By tin and hydrochloric acid it is decolorised, and reconverted into paramidophenol. By sulphurous acid or sodium-hydrogen sulphite it is converted into orthoamidophenolsulphonic acid:



Nitroquinone, $\text{C}^6\text{H}^3(\text{NO}_2)\text{O}_2$, is prepared by dropping chromyl chloride into nitrobenzene at 150°–160° as long as hydrogen chloride is thereby evolved; then adding water; boiling the aqueous solution with a slight excess of alkali; filtering from chromic oxide; concentrating; adding a small quantity of sulphuric acid; and crystallising the resulting precipitate from boiling water. Nitroquinone is thus obtained in shining scales melting at 232°, subliming at a somewhat higher temperature, and dissolving without alteration in alkalis (Etard, *Compt. rend.* lxxxiv. 391).

Dinitro-dihydroxyquinone, or *Nitrannilic acid*, $\text{C}^6\text{H}^2\text{N}_2\text{O}_8 = \text{C}^6(\text{NO}_2)_2(\text{OH})_2\text{O}_2$, and *Tetranitroquinone*, or *Nitrannil*, $\text{C}^6(\text{NO}_2)_4\text{O}_2$ (Nietzki, *Ber.* x. 2147).—When nitrous acid is passed into a well-cooled solution of quinol, a crystalline mass of quinhidrone is formed at first by oxidation of the quinol. Subsequently, however, this body disappears, and small golden-yellow needles separate, easily soluble in ether, but insoluble in water. These needles are converted by potash into sulphuretted potassium-nitrannilate, $\text{C}^6(\text{NO}_2)_2(\text{OK})_2\text{O}_2$.

The yellow crystals soluble in ether probably consist of tetranitroquinone or nitrannil, as they are readily decomposed in ethereal solution by addition of water, with evolution of red fumes, and formation of nitrannilic acid.

Nitrannilic acid crystallises in golden-yellow prisms exhibiting a bluish dichroism; it melts in its water of crystallisation at a little above 100°, and when anhydrous, decomposes without melting at 170°. It has a strong, sour, astringent, ferruginous taste, and forms well crystallised salts with most of the metals, giving crystalline precipitates with barium chloride, calcium chloride, and silver nitrate.

In addition to nitrannilic acid, other nitro-compounds seem to be formed in the reaction above described, together with a considerable quantity of oxalic acid.

Quinhydrone. This body was originally regarded by Wöhler and by Laurent as a compound of 1 mol. quinol and 1 mol. quinone: $\text{C}^6\text{H}^6\text{O}_2 + \text{C}^6\text{H}_4\text{O}_2 = \text{C}^{12}\text{H}^{10}\text{O}_4$. Wichelhaus, on the other hand, regards it as a compound of 2 mols. quinone and 1 mol. quinol: $\text{C}^6\text{H}^6\text{O}_2 + 2\text{C}^6\text{H}_4\text{O}_2 = \text{C}^{18}\text{H}^{14}\text{O}_8$ (vii. 1037). Liebermann, however, has shown (*Ber.* x. 1614, 2000) that quinone and quinol, when brought together in equal numbers of molecules, combine *without residue*, and produce quinhydrone, whereas when 2 mols. quinol and 1 mol. quinone are mixed, half the quinone remains uncombined, and quinhidrone is formed in quantity corresponding with the quinol. These results are in complete accordance with the older formula of quinhydrone, viz.

$C^8H^{10}O^4$; and this formula is further corroborated by the experiments of Nietzsche (*Ber. x.* 2003), who has tested it by reducing quinhidrone with sulphurous acid, and titrating the excess of the latter with iodine solution. Wichelhaus, however (*ibid.* 1781), still endeavours to defend his own formula.

QUINYL OXIDE, $C^8H^{10}O^3 = (C^8H^9OH)^2O$. *Quinolic Ether*.—This compound is formed by the action of chromyl chloride on phenol, and decomposition of the product with an aqueous alkali. Chromyl chloride acts on phenol with great violence, but the action may be moderated by dissolving the two substances (1 pt. C^6H^6O : 5 pts. CrO^2Cl^2) in carbon sulphide. When the action is finished, water is added, and the aqueous solution is boiled with a slight excess of alkali, then filtered, concentrated, and mixed with a small quantity of sulphuric acid. Quinyl oxide is a white amorphous powder, which softens at 100° , and is converted by chromic acid mixture into quinone (Etard, *Compt. rend.* lxxxiv. 391).

R.

RADICLES. A. Cayley has estimated the number of possible isomeric alcohol-radicles of the fatty series as far as C^{13} , and finds 1 Methyl, 1 Ethyl, 2 Propyls, 4 Butyls, 8 Pentyls, 17 Hexyls, 39 Heptyls, 89 Octyls, 211 Nonyls, 507 Decyls, 1238 Undecyls, 3057 Dodecyls, 7638 Tridecyls (*Phil. Mag.* [4], xlvii. 444; [5], iii. 34).

RAFFINOSE, $C^{18}H^{32}O^{16}, 5H^2O$. A substance found in the molasses of the sugar-beet. It is crystalline, colourless, easily soluble in water, sparingly in alcohol, has a very faint sweet taste, gives off water when heated (D. Loiseau, *Compt. rend.* lxxxii. 4058).

RAIZ DEL INDICO. The root of a plant growing in California, and used there in medicine; it contains chrysophanic acid, aporetin, phæoretin, erythroretin, calcium malate and oxalate, starch, gum, sugar, tannin, and albumin (F. G. Voelcker, *Pharm. J. Trans.* [3], vi. 781).

RATANHINE, $C^{10}H^{13}NO^3$. This substance, homologous with tyrosine, first obtained by Wittstein from rhatany-root, and described by Ruge (v. 77), has been further examined by Gintl (*Wien. Akad. Ber.* [2], lx. 668). It unites both with bases and with acids. The *potassium* and *sodium salts*, $C^{10}H^{11}K^2NO^3$ and $C^{10}H^{11}Na^2NO^3$, are amorphous deliquescent masses, partly soluble in alcohol, decomposed by carbonic acid. The *barium salt*, $(C^{10}H^{11}NO^3)^2Ba + 2H^2O$, is a gummy mass having a faint yellow colour. The *strontium salt*, $(C^{10}H^{11}NO^3)^2Sr + 2H^2O$, the *calcium salt*, $(C^{10}H^{11}NO^3)^2Ca (+aq?)$, and the *magnesium salt*, $(C^{10}H^{11}NO^3)^2Mg$, are likewise amorphous. No definite compounds were obtained with aluminium, iron, or lead. The *silver salt*, $C^{10}H^{11}Ag^2NO^3$, prepared like silver-tyrosine (v. 933), is a heavy white precipitate, consisting of microscopic spiculae, slightly soluble in cold water, dissolving with partial decomposition in hot water, easily soluble in ammonia and nitric acid. The ammoniacal solution quickly decomposes, with separation of metallic silver. It remains unaltered at 110° , but burns away at a higher temperature, with a glimmering light, leaving a mixture of silver carbide and spongy charcoal.

Ratanhine is dissolved by organic acids, but soon separates from the solutions. All its compounds with acids are decomposed by alcohol, especially on addition of ether. It dissolves in cold dilute nitric acid, forming the compound $C^{10}H^{13}NO^3.NO^3H$; strong nitric acid converts it into a resinous body which detonates when heated in the dry state. The colour-reaction with nitric acid (red, changing to indigo-blue, v. 78) is most strikingly exhibited with red fuming nitric acid. The product is decolorised by hydrogen sulphide in weak alkaline solution, the characteristic red colour being restored on addition of acids. The *hydrochloride*, $C^{10}H^{13}NO^3.HCl$, crystallises in monoclinic prisms, dissolves at a gentle heat in a small quantity of water, but is decomposed by a larger quantity. The *platinochloride*, $(C^{10}H^{13}NO^3.HCl)^2PtCl^4$, is obtained by slow evaporation of a solution of the hydrochloride mixed with excess of platinic chloride, in small reddish-yellow crystals resembling potassium dichromate; it is permanent in the air, and dissolves without decomposition in water and in alcohol, sparingly also in ether. The *sulphate*, $C^{10}H^{13}NO^3.SO^4H^2$, is obtained in colourless rhombic crystals, by dissolving ratanhine in dilute sulphuric acid and evaporating; it may also be prepared by the action of strong sulphuric acid at ordinary temperatures. The *phosphate*, $C^{10}H^{13}NO^3.PO^4H^2$, is obtained in small prisms,

apparently rhombic, by dissolving ratanhine in moderately concentrated phosphoric acid, evaporating the solution to a syrup, and leaving it at rest for a considerable time.

Ratanhine is not decomposed by nascent hydrogen, either in acid or in alkaline solution (Gintl).

B. Kreitmair (*Liebig's Annalen*, clxxvi. 64) has examined numerous samples of rhatany-extract, some occurring in commerce, others prepared by himself, and has found ratanhine in only one, to the amount of 7 per cent.

RAUTE. A zeolite from the island of Lamö, near Brevig in Norway. It is related to thomsonite, and has probably been formed by decomposition of *elæolite*. It is greyish-black, fine-grained, exhibits no crystalline forms. Hardness 5. Sp. gr. 2.48 at 13°. The mineral encloses small quantities of hornblende, &c. Its analysis gave:

SiO^2	Al^2O^3	Fe^2O^3	CaO	Na^2O	H^2O
39.21	31.79	0.57	5.07	11.55	11.71 = 99.90

numbers which may be represented by the formula $(\text{Na}^2, \text{Ca})\text{O}, \text{Al}^2\text{O}^3, 2\text{SiO}^2, 2\text{H}^2\text{O}$, in which $\text{Na}^2 : \text{Ca} = 2 : 1$ (Paykull, *Ber.* vii. 1334).

REICHARDTITE. This name is given by G. Krause (*Arch. Pharm.* [3], vi. 41) to a massive variety of magnesium sulphate, $\text{MgSO}^4 + 7\text{H}^2\text{O}$, occurring at Stassfurt.

RESINS. The behaviour of the more important resins, gum-resins, and balsams with various reagents, has been examined by E. Hirschsohn (*Russ. Zeitschr. Pharm.* xvi. 1, 33, 65, 97; *Arch. Pharm.* [3], x. 481; xi. 54, 152, 247, 312, 434), with the following results:

Alcohol of 95 per cent. dissolves completely:

Benzoïn, Caranna, Resins and Balsams from Conifers, Dragon's-blood, Guajacum, Peruvian guajacum, Mani-resin, Mastic from Alexandria, Mastic from Bombay, Black Peru-balsam, Podocarpus-resin, Sandarac, Tolu-balsam, Xanthorrhœa-resins.

Alcohol of 95 per cent. dissolves incompletely:

Ammoniacum, Asa fetida, Bdellium, Canada-balsam, Ceradia-resin, Copaiba-balsam, Copal, Dammar, Elemi, Euphorbium, Resin of *Euphorbia Tirocalli*, Euryops-resin, Galbanum, Gamboge, Shellac, Liquidambar-balsam, common Mastic, Mecca-balsam, Myrrh, Olibanum, Opoponax, white Peru-balsam, Sagapenum, Sonora-lac, Liquid Storax.

Ether dissolves completely:

Caranna, Canada-balsam, Conifer-resins and balsams, Copiba-balsam, Dragon's-blood, Elemi, Guajac-resin, Peruvian guaiac, Mani-resin, Mastic, Podocarpus-resin, Sandarac.

Ether dissolves incompletely:

Ammoniacum, Asa fetida, Bdellium, Benzoïn, Ceradia-resin, Copal, Dammar, Euphorbium, Resin of *Euphorbia Tirocalli*, Euryops-resin, Galbanum, Shellac, Gamboge, Liquidambar-balsam, Mecca-balsam, Myrrh, Olibanum, Opoponax, black Peru-balsam, white Peru-balsam, Sagapenum, Sonora-lac, Liquid Storax, Tolu-balsam, Xanthorrhœa-resins.

Ethereal solution clouded by addition of Alcohol:

Canada-balsam, Brazilian Copal, Copaiba-balsam from Maranhão and from Pará, Dammar, Resin of *Euphorbia Tirocalli*, Euryops-resin, Liquidambar-balsam, common Mastic, white Peru-balsam, Sonora-lac, Liquid Storax.

Ethereal solution forms a clear mixture with Alcohol:

Ammoniacum, Asa fetida, Bdellium, Benzoïn, Caranna, Ceradia-resin, Conifer-resins and balsams, Copaiba-balsam from Brazil, Copal, Dragon's-blood, Elemi, Euphorbium, Guajacum, Peruvian guajacum, Galbanum, Shellac, Gamboge, Balsam of *Liquidambar styraciflua*, Mani-resin, Mastic from Bombay, Mastic from Alexandria, Mecca-balsam, Myrrh, Opoponax, black Peru-balsam, Podocarpus-resin, Sandarac, Sagapenum, Tolu-balsam, Xanthorrhœa-resins.

Chloroform dissolves completely:

Benzoïn, Canada-balsam, Caranna, Ceradia-resin, Conifer resins and balsams, Copaiba-balsam, Brazilian Copal, Dammar, Dragon's-blood (not all varieties), Guajac-resin, Peruvian guaiac, Mani-resin, Mastic, Mecca-balsam, black and white Peru-balsam, Tolu-balsam.

Chloroform dissolves imperfectly or not at all:

Ammoniacum, Asa fetida, Bdellium, Copal, Dragon's blood from *Pterocarpus Draco*, Euphorbium, Resin of *Euphorbia Tirocalli*, Euryops-resin, Galbanum, Shellac, Gamboge, Liquidambar-balsam, Myrrh, Olibanum, Opoponax, Podocarpus-resin, Sagapenum, Sandarac, Sonora-lac, Liquid Storax, Xanthorrhæa-resins.

Lead Acetate gives with the Alcoholic solution a precipitate which does not dissolve or dissolves only partially on boiling:

Ammoniacum, common Asa fetida, Benzoin, Canada-balsam, Caranna, Ceradia-resin, Conifer-resins and balsams, Copal, Dammar (certain East Indian samples), Galbanum, Euphorbium, Resin of *Euphorbia Tirocalli*, Dragon's blood from *Pterocarpus Draco*, Shellac, Guajacum, Mani-resin, Mastic from Bombay, common Myrrh, black Peru-balsam, Sandarac, Sonora-lac, Liquid Storax, Tolu-balsam, Resin of *Xanthorrhæa arborea*, yellow Xanthorrhæa-resin.

Lead Acetate gives a turbidity which disappears on heating:

African Bdellium, Copaiba-balsam, Dammar (certain East Indian samples), Peruvian Guajacum, Balsam of *Liquidambar styraciflua*, common Mastic, Mastic from Alexandria, Mecca-balsam.

Lead Acetate gives no turbidity:

Asa fetida from *Perula alliacea* Boiss, Indian Bdellium, Caranna (*Aceyta americana*), Dammar, Dragon's blood (some sorts), Elemi, Gamboge, Liquidambar-balsam, Indian Myrrh, Olibanum, Podocarpus-resin, white Peru-balsam, Resin of *Xanthorrhæa quadrangularis*.

Ferric Chloride gives with the Alcoholic solution a turbidity or a precipitate which disappears on heating, and dissolves in ether:

Canada-balsam, Dammar (some East Indian sorts).

Ferric Chloride gives a precipitate which neither disappears on heating nor dissolves in ether:

Copal, Sonora-lac.

Ferric Chloride gives no precipitate, but colours the solution:

(a). *Blue*: Caranna (*Aceyta americana*), Guajacum. (b). *Black, brown-black, or greenish-black*: Gamboge, Xanthorrhæa-resins, Shellac. (c). *Dark green*: Asa fetida (some sorts), Benzoin. (d). *Black*: Peru-balsam, Storax-balsam, Opoponax, Sagapenum.

The other resins are coloured by ferric chloride either greenish, brownish, or not at all.

Aqueous Ammonia forms with the Alcoholic solution a clear mixture:

Caranna, Ceradia-resin, Conifer-resins (some sorts), Copal, Dragon's blood from *Pterocarpus Draco*, Euryops-resin, Shellac, Guajacum, Gamboge, Podocarpus-resin, Sandarac, Sonora-lac, Xanthorrhæa-resins.

Aqueous Ammonia forms a turbid mixture:

The remaining Resins.

Chloride of Lime Solution gives an orange-yellow colour with: Persian ammoniacum; no colour with any of the other resins.

Alcohol containing Hydrochloric acid is coloured brick-red by: white Peru-balsam, Ceradia-resin; red to violet by: Caranna (one sample), common Myrrh, Euryops-resin; blue to violet by: Elemi (some sorts); yellowish-brown to green: Guajacum-resin; yellow changing through red-brown to cherry-red: Benzoin, Tolu-balsam; crimson: Resin of Xanthorrhæa arborea and X. quadrangularis; greenish changing to dingy violet: common Asa fetida; yellow: Gamboge, Caranna; light rose-coloured: Podocarpus-resin; brown changing into various shades: the remaining resins.

Concentrated Sulphuric acid dissolves with cherry-red colour: Benzoin from Siam, Tolu-balsam; yellow: Gamboge; with yellowish-brown fluorescence: common Asa fetida; brown changing to various shades: the rest.

The solution in Sulphuric acid gives with Alcohol a clear violet mixture: Benzoin from Siam, benzoin from Sumatra (more red-violet), Euryops-resin, Levant Galbanum, Tolu-balsam; blue-violet changing to blue: Levant Sagapenum; a clear cherry-red mixture: red Xanthorrhæa-resin; a clear green mixture: Guajacum, yellow Xanthorrhæa-resin; a turbid dingy violet mixture: Myrrh, black Peru-balsam; a turbid brown mixture: the other resins.

Water added to the sulphuric acid solution throws down resin in flocks, and

exhibits a violet colour: Benzoin from Siam; *dingy red-violet*: black Peru-balsam, Galbanum, African Ammoniacum, Sagapenum, Benzoin from Sumatra, Tolu-balsam, red Xanthorrhæa-resin; *yellow*: Gamboge; *blue-green or black-blue*: Guajacum; *brown*: the other resins.

Bromine-solution, added to the chloroform extract, produces either immediately or after some time a *red colour*: Peruvian Guajacum; *cherry-red*: white Peru-balsam; *red-violet*: common Myrrh, Caranna (one sample), resin of *Xanthorrhæa arborea*; *yellowish changing to violet and blue*: Copaiba-balsam from Maranhão and Para; *blue*: Guajacum, Caranna, Ceradia-resin, Euryops-resin; *brown*: the rest.

Bromine-solution, added to the chloroform-extract, throws down the resin in flocks: Shellac, Australian Copal.

Sodium Carbonate solution at ordinary temperatures is coloured *violet* by Shellac; *crimson* by Sonora-lac; *yellowish or yellow-red* by common Asa fœtida, Dragon's-blood from *Pterocarpus Draco*, Euphorbium, Guajacum (*greenish* at first), Gamboge, Xanthorrhæa-resins; *yellowish, brownish, or not at all* by the rest.

Sodium Carbonate solution at boiling heat is coloured *violet* by Shellac; *yellow* by Asa fœtida, Benzoin, Euphorbium, Dragon's-blood, Guajacum, black Peru-balsam, Sandarac, Storax-balsam, Xanthorrhæa-resins; *yellowish, brownish, or not at all* by the rest.

From the extracts obtained with sodium carbonate at ordinary temperatures, Acetic acid throws down flocks: Conifer-resins and balsams, Guajacum, Gamboge, Podocarpus-resin, Sandarac, Xanthorrhæa-resins. Acetic acid throws down nothing or produces only a slight turbidity: the rest.

Umbelliferone is obtained by the dry distillation of: Asa fœtida, African Ammoniacum, Galbanum, Sagapenum.

Sulphur may be detected in Asa fœtida, Bdellium, some sorts of Caranna and Dragon's-blood.

Cinnamic acid is contained in Benzoin from Sumatra, Dragon's-blood, Liquidambar-balsam, black Peru-balsam, Tolu-balsam, red Xanthorrhæa-resin.

The Petroleum-ether extract is coloured *deep yellow* in the case of Gamboge, Euryops-resin; *dark brown*: Mani-resin; *yellowish or colourless*: the rest.

Iodine-solution gives with the petroleum-ether extract a *clear violet mixture*: Benzoin, Indian Bdellium, Dragon's-blood, Shellac, Guajacum, Galbanum, Peruvian Guajacum, Indian Myrrh, yellow Xanthorrhæa-resin, resin of *Xanthorrhæa quadrangulare*; *red violet mixture*, clear at first, but afterwards becoming turbid: Copal, Dammar (some samples), Mastic, Gamboge, black Peru-balsam, Podocarpus-resin, Sandarac, Storax-balsam, resin of *Xanthorrhæa arboracea*; *brown and turbid mixtures*: the rest.

Sulphuric acid colours the evaporation-residue of the Petroleum-ether extract *crimson*: Benzoin from Siam, Guajacum; *no coloration*: Shellac, Podocarpus-resin; *yellow or brown*: the rest.

Chloral-reagent* colours the residue gradually *violet*: common Myrrh, Caranna, Euryops-resin; *crimson changing to violet*: white Peru-balsam; *rose-coloured changing to violet*: Levantine Galbanum (old commercial sample), Levantine Sagapenum; *yellowish or greenish changing to red-violet*: Canada-balsam, Conifer-resins and balsams; *yellow*: Caranna, Gamboge; *green*: Dammara viridis, Persian Galbanum, Mecca-balsam, Persian Sagapenum; *dull green with rose-coloured edges*: Levantine Galbanum (sort at present occurring in commerce); *greenish*: Asa fœtida, Indian Bdellium, Benzoin from Sumatra, Persian Ammoniacum, Liquidambar-balsam, black Peru-balsam; *blue into violet*: balsam of Liquidambar styraciflua; *no coloration or very faint*: the rest.

The evaporation-residue after being heated to 120° is either soft or fluid: Asa fœtida, Benzoin from Sumatra, Liquidambar-balsam, Opoponax, black Peru-balsam, Tolu-balsam, Sagapenum, Storax-balsam.

Colophony. Processes for separating common resin, or colophony, from fatty acids, are described by C. Barfoed (*Zeitschr. anal. Chem.* 1875, 20; *Chem. Soc. J.* xxix. 771). For qualitative examination, the following methods may be adopted: 1. The mixture is dissolved, with aid of heat, in alcohol of 70 per cent. and then left to cool, whereupon the fatty acids separate out while the resin remains dissolved. 2. The mixture is heated with an alcoholic solution of sodium carbonate (7 vols. spirit of 30 per cent. and 1 vol. of a solution of 1 pt. crystallised sodium carbonate in 3 pts. water) till it is dissolved, and then left to cool, whereupon the sodium salts of the

* An impure chloral hydrate obtained by saturating alcohol with chlorine, mixing the product with 4 vols. strong sulphuric acid, stirring up the solid mass which separates with one-third of its weight of water, and distilling.

fatty acids separate, while the sodium resinate remains dissolved. 3. The mixture dissolved in alcohol is mixed with an alcoholic solution of calcium chloride and ammonia. The fatty acids then separate as calcium salts, while the calcium resinate remains dissolved in the alcohol. 4. The mixture is dissolved in the requisite quantity of soda-ley, the solution evaporated to dryness on the water-bath, and the residue treated with a mixture of 1 vol. alcohol of 98 per cent. and 5 vols. ether; in this case only the sodium resinate is dissolved. If any notable quantity of oleic acid is present, together with the stearic and palmitic acids, complete separation can be effected only by the fourth method, care being taken also that the solution containing soda be evaporated to complete dryness, and that the ether-mixture be prepared with absolute alcohol and ether.

The fourth method may be advantageously employed for quantitative estimation.

Colophthalin, $C^{11}H^{10}$. This name is given by P. Curie (*Chem. News*, xxx. 189) to a solid hydrocarbon occurring amongst the products of the dry distillation of colophony. It is prepared by heating 100 pts. colophony with 50 p.s. sulphur at 400° , and purifying the distillate with cold alcohol. Pure colophthalin is a white flocculent body having a faint balsamic odour, easily soluble in benzene, turpentine-oil, carbon bisulphide, ether, boiling alcohol, and boiling glacial acetic acid; it melts at 70° and boils at 400° . By oxidising agents it is converted into oxycolophthalin, $C^{11}H^{10}O$, by chlorine into chlorocolophthalin, $C^{11}H^8Cl^2$; by hot nitric acid i to nitrocolophthalin, which, when boiled with alkaline leys, gives off all its nitrogen as ammonia, and is converted into a compound called by Curie, colophulmic acid. These derivatives of colophthalin, when fused with caustic potash, yield a substance resembling alumina, and called colophalumina, which is insoluble in water, alcohol, and ether, infusible, non-volatile, and is said not to be decomposed by chlorate or nitrate of potassium even at 1000° . Curie represents its composition by the formula $C^{10}H^8O^2$. By chlorine at a red heat, it is converted into chlorocolophalumina, $C^{10}H^6Cl^2O^2$, and by fusion with potash into colophaluminic acid, $C^{10}H^6O^4$.

RESORCINOL, $C^6H^4(OH)^2$ [1 : 3]. This compound is formed by the action of melting potash on all the three modifications of monobromophenol (Fittig a. Mager, *Ber.* viii. 362), in like manner from *p*-chlorophenol (Faust, *Ber.* vi. 1022), and from *p*-iodophenol at temperatures above 165° (Nölting a. Wrzesinski, *ibid.* 820). Its formation from para- and ortho-derivatives must take place by atomic transposition, and shows that resorcinol is the most stable of the three modifications of dihydroxy-benzene. Nölting a. Wrzesinski find, indeed, that para-iodophenol, when fused with potash, yields quinol at 165° , and resorcinol at higher temperatures. Resorcinol is also formed by the action of sodium-amalgam on paramorin, and, together with the latter, by the dry distillation of morin (p. 1337); further, together with protocatechuic acid and volatile fatty acids, by the action of melting potash on hydrocarotin (Brimmer, *N. Rep. Pharm.* xxiv. 641).

On the preparation of Resorcinol from Brazilin, see vii. 1040.

On the manufacture of Resorcinol, Eosin, and other resorcinol-derivatives, see Bindschedler a. Busch (*Chem. News*, xxxviii. 226; *Chem. Soc. J.* xxxvi. 291).

Resorcinol is most readily purified by crystallisation from pure anhydrous benzene. It dissolves easily therein when heated, and crystallises almost completely on cooling in large transparent perfectly colourless needles, or by spontaneous evaporation in very large well-developed rhombic prisms, having the aspect of crystals of nitre or urea (Fittig a. Mager, *Ber.* vii. 1177; viii. 365).

According to Calderon (*Compt. rend.* lxxxiv. 779), the crystals of resorcinol are orthorhombic, and exhibit the combination ∞P . $\bar{P}\infty$; or sometimes ∞P . $\infty \bar{P}2$. $\bar{P}\infty$. Axes $a : b : c = 0.912326 : 1 : 1.0587577$. The crystals are often elongated in the direction of the axis a , and have sometimes the appearance of a perfect octohedron. Resorcinol melts at 118° , boils at 276.5° under a pressure of 759.7 mm., between 200° and 210° under a pressure of 7 mm., and decomposes at 300° . Its vapour-density, determined by Dumas' method under reduced pressure, gave, as a mean of two experiments, 3.862 instead of the theoretical number 3.8078. The density of solid resorcinol, taken in carbon sulphide, was found to be 1.2728 at 0° , 1.2717 at 15° . Coefficient of expansion, 0.00007868 between 0° and 15° ; for the liquid between 118° and 178° , uniformly 0.0007114. The molecular volume calculated for liquid resorcinol between 118° and 178° varies from 92.26 (at 118°) to 96.196 (at 178°). Calculation gives for the molecular volume of liquid-resorcinol at 0° , the number 86.43, and for the solid 85.13, showing a difference of 1.3; the molecular volume at the boiling point is 103.17. A comparison of the molecular volumes of resorcinol, phenol, and benzene at 100° gives the following results:

	Sp. gr.	Mol. volume
Benzene	0.7938	98.26
Phenol	1.0128	92.9
Resorcinol	1.2076	9.109

For the densities of solutions of resorcinol containing $\frac{1}{2}$, 1, and $1\frac{1}{2}$ eq. in a litre, Calderon (*Compt. rend.* lxxiv. 1164) finds the following numbers—

Content in 1 l.	at 0°	at 10°	Density at 100°
$\frac{1}{2}$ eq.	1011.48	1011.11	964.05
1 eq.	1023.17	1023.23	976.64
$1\frac{1}{2}$ eq.	1034.06	1033.32	987.41

Reactions. 1. *Oxidation.*—Resorcinol is oxidised by fusion with soda, and on dissolving the melt in dilute sulphuric acid, exhausting the acid solution with ether, and evaporating the latter, phloroglucinol, $C^6H^3O^3$, crystallises out to the amount of 60–70 per cent. of the resorcinol. The mother-liquor yields with lead acetate a yellow precipitate, which, when decomposed by hydrogen sulphide, yields a syrupy liquid, decomposing when distilled, with formation of catechol. The filtrate from the lead precipitate contained a small quantity of unaltered resorcinol, but consisted chiefly of phloroglucinol and tetroxydiphenyl, $C^{12}H^{10}O^4$, in the form of a crystalline powder or long colourless needle-shaped crystals not melting at 250° (Barth a. Schreder, *Ber.* xii. 503).

2. Resorcinol subjected to exhaustive chlorination in a stream of *chlorine*, with addition of a little *iodine* (p. 1066), yields perchloromethane, CCl_4 , together with carbon dioxide (Ruoff, *Ber.* x. 1483). 3. Treated in aqueous solution with *iodine chloride* till iodine separates out, it is converted into tri-iodoresorcinol, together with a brown substance insoluble in carbon sulphide (Michael a. Norton, *Ber.* ix. 1752). 4. *Sulphuryl chloride*, SO_2Cl_2 , converts resorcinol into mono- and di-chlororesorcinol (p. 1748). 5. With *chloroform* and a caustic alkali, it yields resorcinol aldehydes (p. 1751). 6. Resorcinol, heated to 150° – 160° with strong *sulphuric acid*, is converted into resorcinoldisulphonic acid; at 200° with *fuming sulphuric acid*, into resorcinoltrisulphonic acid (Piccard a. Humbert, p. 1752). J. Annaheim (*Ber.* x. 975), by heating resorcinol (22 pts.) with fuming sulphuric acid (9.8 pts.) for an hour or two at 120° – 130° , obtained a deep red substance, changing as it cooled to a solid mass having a green metallic reflex. On boiling it with water, the greater part remained undissolved in the form of a resinous sulphuretted body, which dissolved with red colour in alcohol, glacial acetic acid, and alkalis, the solutions, especially that in ammonia, exhibiting a splendid fluorescence. The red colouring matter may be separated from the alcoholic solution by water, and from the alkaline solutions by acids. With bromine and iodine it forms compounds which are likewise fluorescent. 7. When 1 mol. resorcinol and 2 mols. *oxalic acid* are heated together in a sealed tube at 200° for two or three hours, a mass is formed which, when diluted with a little alcohol and poured into water, yields a flocculent precipitate purifiable by solution in alcohol and reprecipitation by water. This substance, which has the composition $C^{13}H^4O^4$, and may perhaps be represented by the constitutional formula $C^6H^3O.CO.C^6H^3(OH)^2$, is a fine red powder, very hygroscopic, easily soluble in alkalis with green fluorescence, soluble also in glacial acetic acid and in alcohol, and precipitated unchanged from its alkaline solution by acids. It has not been obtained in the crystalline state. Acetic anhydride converts it on boiling into an acetyl-derivative, $C^{13}H^7(C^2H^3O)O^4$. A brominated derivative is formed by adding bromine to its alkaline solution (Claus a. Andreae, *Ber.* x. 1305).

8. Resorcinol, treated with *oxalic acid* in presence of dehydrating agents (sulphuric acid, phosphoric anhydride, glycerol), yields two colouring matters having the composition $C^{14}H^3O^5$, one of which is light yellow, insoluble in alcohol, easily dissolved by potash-ley, forming a solution which exhibits green fluorescence, while the other is a dark brown mass, soluble in alcohol, and dissolving in potash-ley with brown colour but without the slightest fluorescence (Gukassianz, *Ber.* xi. 1184).

9. A solution of resorcinol, mixed with *cupric sulphate*, yields, on addition of ammonia in quantity sufficient to redissolve the precipitate at first produced, a deep black liquid with which wool and silk may be dyed black (R. Wagner, *Dingl. pol. J.* cxx. 96).

10. Resorcinol introduced into the animal organism is converted into a sulphonic acid, which is eliminated in the urine (Baumann a. Herter, *Ber.* ix. 1747; *Zeitschr. physiol. Chem.* i. 244).

Bromoresorcinols. These compounds have been studied by Liebermann a. Dittler (*Ber.* v. 1090, and this Dictionary, vii. 1042), and further details respecting

them are given by the same authors in a later communication (*Liebig's Annalen*, clxix. 252).

Pentabromoresorcinol, $C^6HBr^5O^2$, crystallises, according to Rammelsberg's measurements, in the dimetric or quadratic system, exhibiting the combination $\infty P \infty . 0P . P$. Axial ratio $a : c = 0.6076 : 1$. Angle $P : P' = 98^\circ 58'$; $P' : P = 133^\circ 30'$; $P : 0P = 113^\circ 15'$; $P : \infty P = 130^\circ$. The faces $\infty P \infty$ are small and incomplete in number.

The liquid obtained by dissolving colourless pentabromoresorcinol in cold alcohol is yellow, as if from separated bromine, and on adding to it an aqueous solution of potassium iodide and then carbon sulphide, the latter immediately becomes purple, as from separated iodine. When an alcoholic solution of silver nitrate is added by drops to an alcoholic solution of pentabromoresorcinol, rather more than 1 mol. bromine is thrown down as silver bromide from 1 mol. pentabromoresorcinol.

Tribromoresoquinone, $C^6HBr^3O^2$ (vii. 1042), formed by heating pentabromoresorcinol at 150° – 160° , is insoluble in water, easily soluble in alcohol, sparingly in ether, carbon sulphide, benzene, and chloroform, and crystallises therefrom in needles. It decomposes at 190° , but remains for the most part unaltered when treated with sodium-amalgam, or when sulphur dioxide is passed into its alcoholic solution heated to 50° – 60° . It resinises when heated with aqueous sulphurous acid at 140° , and with hydriodic acid at a higher temperature. It unites with 1 mol. bromine, reproducing pentabromoresorcinol (Liebermann & Dittler).

From experiments by H. Claassen (*Ber.* xi. 1438), it appears that of the five bromine-atoms in pentabromoresorcinol, three are more stable or less easily removed than the other two: thus pentabromoresorcinol boiled with *formic acid* yields CO^2 , HBr, free bromine, and tribromoresorcinol; with aldehyde, it yields HBr and tribromoresorcinol; and with *acetic anhydride*, tribromodiacetylresorcinol, $C^6HBr^3(OC^2H^3O)^2$. This fact of the easier removal of two out of the five bromine-atoms in pentabromoresorcinol, renders it probable that this compound is correctly represented by the formula $C^6HBr^4(OBr)^2$.

Pentabromoresorcinol is converted by reduction with tin and hydrochloric acid first into tribromoresorcinol, $C^6HBr^3(OH)^2$, then into resorcinol; with *aniline* it yields tribromoaniline and tribromoresorcinol; with *phenol*, tribromoresorcinol and tribromophenol (Benedikt, *Ber.* xi. 1599).

Tetrabromoresorcinol, $C^6Br^4(OH)^2$, formed by heating pentabromoresorcinol with strong sulphuric acid, melts at 163° , dissolves readily in hot alcohol, ether, chloroform, and alkalis, sparingly in water, and when boiled with acetic anhydride, yields tetrabromodiacetylresorcinol, $C^6Br^4(OC^2H^3O)^2$, which is insoluble in water, easily soluble in hot alcohol and in ether, and melts at 169° .

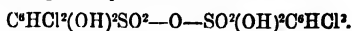
Tribromomonoacetyl-resorcinol, $C^6HBr^3(OH)(OC^2H^3O)$, is prepared by treating 1 pt. diacetyl-resorcinol with 5 pts. bromine and 40 pts. water, and separates from solution in carbon sulphide in small transparent crystals, which melt at 114° , and are converted by boiling with aqueous potash into tribromoresorcinol, and by acetic anhydride into tribromodiacetyl-resorcinol, $C^6HBr^3(OC^2H^3O)^2$.

Tetrabromodiresorcinol, $C^{12}H^2Br^4(OH)^4 = (OH)^2HBr^2C^6 - C^6Br^2H(OH)^2$, prepared by boiling tribromoresoquinone with tin and hydrochloric acid, crystallises from glacial acetic acid in rose-red needles, easily soluble in alcohol and ether, decomposing at 280° , and reduced by sodium-amalgam to an amorphous non-brominated compound which, when distilled over zinc-dust, yields diphenyl (Benedikt, *Ber.* xi. 2168).

Chloro-resorcinols (Reinhard, *J. pr. Chem.* [2], xvii. 321; Claassen, *Ber.* xi. 1438). **Monochlororesorcinol**, $C^6H^3Cl(OH)^2$, formed by adding an equivalent amount of sulphuryl chloride, drop by drop, to resorcinol dissolved in absolute ether, and distilling, is a white crystalline body, melting at 89° , but beginning to sublime at 75° , and distilling at 255° – 256° . It is soluble in water, alcohol, ether, benzene, and carbon bisulphide: its aqueous solution slightly reddens litmus paper. It is attacked by warm dilute nitric acid, with evolution of chlorine and nitrous acid, and formation of a hard resinous mass. With ferric chloride it produces a blue-violet colour, becoming brown on heating. It reduces ammoniacal silver solution, and seems to form a very unstable potassium derivative, $C^6H^3Cl(OK)^2$. No derivatives of it could be obtained by fusion with potassium hydrate or cyanide. The action of bromine upon its aqueous solution at 80° gives rise to **monochlorodibromoresorcinol**, $C^6HBr^2Cl(OH)^2$, which crystallises in slender brilliant needles, melting at 105° . The **benzoyl-derivative**, $C^6H^3Cl(OC^2H^3O)^2$, produced by the action of benzoyl chloride upon monochlororesorcinol, crystallises from hot alcohol in small hexagonal needles, melting at 98° , and, when saponified, yields a benzoate and the original monochlororesorcinol.

Dichlororesorcinol, $\text{C}^6\text{H}^2\text{Cl}^2(\text{OH})^2$, is obtained by rubbing together in a basin resorcinol and sulphuryl chloride, in the proportion of 1 to 2 mols., heating after addition of a very little more sulphuryl chloride, and subliming two or three times. It is very soluble in water and other ordinary solvents, and is obtained by evaporation of its aqueous solution over sulphuric acid, in well-formed rhombic prisms, readily efflorescing in air, melting at 77° , and boiling at 249° . **Dichloromonobromoresorcinol**, $\text{C}^6\text{H}^2\text{BrCl}^2\text{O}^2$, is obtained by the action of bromine upon dichlororesorcinol, and the *benzoyl-derivative*, $\text{C}^6\text{H}^2\text{Cl}^2(\text{OC}^7\text{H}^5\text{O})^2$, by the action of benzoyl chloride: the former melts at 100° , the latter at 127° .

Sulphuryl hydroxychloride, $\text{SO}^2\text{Cl}(\text{OH})$, acts energetically on dichlororesorcinol with formation of a white solid, consisting of microscopic rhombic crystals, soluble in potash and in potassium carbonate solution (in the latter case with evolution of carbon dioxide), but insoluble in water, alcohol, and ether. This substance has the empirical formula, $\text{C}^6\text{H}^2\text{Cl}^2\text{S}^2\text{O}^3$, and probably the structural formula,



By decomposing a solution of this body in potassium carbonate with hydrochloric acid, evaporating on the water-bath, and crystallising from alcohol, the corresponding acid, $\text{C}^6\text{HCl}^2(\text{SO}^2\text{H})(\text{OH})^2$, was obtained as a white powder, soluble in water and in alcohol, and decomposed by sulphuryl hydroxychloride into the anhydride and water. The insoluble barium salt was obtained by boiling the anhydride with baryta-water, or by precipitating a solution of the anhydride in potassium carbonate with barium chloride.

Trichlororesorcinol, $\text{C}^6\text{HCl}^3(\text{OH})^2$, is obtained by gradually adding to resorcinol about six times its own weight of sulphuryl chloride, heating for some hours in a flask fitted with a reversed condenser, distilling off the excess of sulphuryl chloride, drying in a vacuum over potash, and repeatedly crystallising from hot water. It forms small brilliant needles, readily soluble in alcohol and in ether, melting at 83° , but subliming only with partial decomposition.

By treating an aqueous solution of resorcinol with excess of chlorine, a trichlororesorcinol was obtained, melting at 73° . Reinhard regards this body as identical with that obtained by the action of excess of sulphuryl chloride upon resorcinol, attributing the difference between the melting points to small amounts of impurities.

Trichlororesorcinol forms a *benzoyl-derivative*, $\text{C}^6\text{HCl}^3(\text{OC}^7\text{H}^5\text{O})^2$, which melts at 133° . Sulphuryl chloride, heated with trichlororesorcinol in a sealed tube, reacts upon it at 160° , probably forming tetrachlororesorcinol, which, however, has not yet been obtained in the pure state (Reinhard).

Pentachlororesorcinol, $\text{C}^6\text{HCl}^5\text{O}^2$, is somewhat more stable than the corresponding bromine-compound (p. 1748), not being altered by heating either alone or in contact with aldehyde or formic acid; a strong solution of acid potassium sulphite, however, converts it into a trichlororesorcinol, which crystallises from water in white needles melting at 69° (comp. Reinhard, *supra*), and dissolving readily in alcohol, ether, and hot water (Claassen).

Tri-iodoresorcinol, $\text{C}^6\text{HI}^3(\text{OH})^2$, is formed, together with a brown substance insoluble in carbon sulphide, when iodine chloride is added to an aqueous solution of resorcinol. It is insoluble in water, moderately soluble in glacial acetic acid, easily in carbon sulphide, alcohol, and ether, and crystallises in long needles having a faint rose-colour, and melting at 145° (uncorr.) When heated above 190° , it sublimes and decomposes, giving off vapours of iodine. By alkalis, alkaline carbonates and aniline, it is dissolved with brown colour and at the same time decomposed (Michael's Norton, *Ber.* ix. 1752).

Dinitrosoresorcinol, $\text{C}^6\text{H}^2(\text{NO})^2(\text{OH})^2$ (A. Fitz, *Ber.* viii. 631). This compound is prepared by adding to 1 mol. resorcinol dissolved in fifty times its weight of water and cooled to 0° , first 2 mols. acetic acid and then rather more than 2 mols. potassium nitrite dissolved in water, whereupon, after a few minutes, the green acid potassium salt of dinitrosoresorcinol begins to separate, perhaps mixed with free dinitrosoresorcinol, to judge by the darkening of the liquid. On pouring the mass, after a quarter of an hour's rest, into 2 mols. dilute sulphuric acid, free dinitrosoresorcinol separates in yellowish flocks, which, after standing for an hour, may be collected on a filter, well washed, and crystallised from water, or better from hot alcohol of 50 per cent. The solution becomes dark from oxidation, and on cooling deposits the nitroso-compound in yellowish-gray, or yellowish-brown, shining crystalline laminae, which have the composition $\text{C}^6\text{H}^2(\text{NO})^2(\text{OH})^2 + 2\text{H}^2\text{O}$, suffer but little loss of weight at 100° , but detonate at 115° . They are but sparingly soluble in cold water, alcohol, methyl alcohol, or acetone, more soluble in these liquids when hot, insoluble in ether and in benzene. From hot alcohol, dinitrosoresorcinol separates in the amorphous state. The hot solutions oxidise very readily when exposed to the air.

Dinitrosoresorcinol is a moderately strong acid, decomposing carbonates completely and acetates partially. Its salts are amorphous, excepting those of potassium, sodium, ammonium, and calcium. The *acid sodium salt* is prepared by drenching dinitrosoresorcinol with a small quantity of water, adding the requisite quantity of soda-ley, and passing carbon dioxide through the solution for some time; the salt then separates in the form of a slightly soluble dark green crystalline powder. The *ammonium salt*, $C^6H^2(NO)_2(OH)(ONH^4)$, is a greenish-brown powder; the corresponding *potassium salt*, a light green, slightly soluble crystalline powder. The other salts are obtained from the acid sodium salt by precipitation, *barium chloride* giving a green precipitate soluble in dilute acetic acid; *calcium chloride* a greyish-green crystalline precipitate, sparingly soluble in water, soluble in dilute acetic acid; *silver nitrate* a grey flocculent precipitate; *lead acetate* a brown-red flocculent precipitate; *cupric sulphate* a brown-red; *zinc sulphate* a flocculent; *mercurous nitrate* a brown-red; *ferrous sulphate* a blue-green precipitate. *Ferric chloride* gives at first a deep green coloration, then a dark green precipitate. The normal alkali-salts are easily soluble; the other salts, both normal and basic, are amorphous and sparingly soluble.

Nitric acid, even when dilute and cold, converts dinitrosoresorcinol into trinitrosoresorcinol; potassium ferricyanide and permanganate raise it to a higher stage of oxidation or burn it up completely. By tin and hydrochloric acid, on the other hand, it is very easily reduced to diamidosorcinol (*infra*). With acetic anhydride, aniline, alcohol and glacial acetic acid, alcoholic hydrochloric acid, and with resorcinol and strong sulphuric or glacial acetic acid when heated, dinitrosoresorcinol forms brown resinous products. Its alcoholic solution is coloured a deeper yellow by nitrous acid, but the compound itself remains unaltered.

Diamidosorcinol, $C^6H^2(NH^2)^2OH$, is formed, as above mentioned, by reducing the dinitroso-compound with tin and hydrochloric acid. The resulting hydrochloride, which acquires a dark brown colour, is best converted into the more stable sulphate, which separates on addition of sulphuric acid, and more quickly if alcohol be likewise added, in slightly coloured needle-shaped crystals having the composition $C^6H^2(NH^2)_2(OH)_2 \cdot SO_4H^2 + 1\frac{1}{2}H^2O$, and giving off their water at 100° . The base, when separated by alkalis, immediately turns brown and decomposes on exposure to the air. With ferric chloride it produces a fine blue colour, quickly changing to dirty brown (Fitz).

Trinitrosoresorcinol, or Styphnic Acid, $C^6H(NO^2)_3(OH)^2$, is formed, together with three dinitrobenzoic acids, when orthonitrobenzoic acid is gradually added to a warm mixture of equal parts of fuming nitric and sulphuric acids (Griess, p. 267). The styphnic acid thus obtained agrees in its melting point (175°) and the composition of its barium salt, $C^6H(NO^2)_3O^2Ba + 3H^2O$ (small yellow rhombic prisms very slightly soluble, even in boiling water, and giving off their crystallisation-water at 200°) with that described by Stenhouse (vii. 1044). H. Salkowski (*Ber.* viii. 637), on repeating the nitration of orthonitrobenzoic acid in the manner described by Griess, obtained a barium salt of styphnic acid containing only 1 mol. H^2O , and crystallising in small orange-coloured scales, nearly insoluble in water even at the boiling heat.

Merz a. Zetter (*Ber.* xii. 681) prepare trinitrosoresorcinol by heating resorcinol with excess of sulphuric acid at 100° , and adding to the resulting sulphonic acid first slightly diluted, then concentrated nitric acid, and finally an excess of fuming nitric acid. On pouring the product after a while into cold water, the trinitro-compound is thrown down in the pure state. Trinitrosoresorcinol is also formed by prolonged boiling of ostruthin with dilute nitric acid (Gorup-Besanez, *Liebig's Annalen*, clxxxiii. 321), and in theoretical quantity by the continued action of strong nitric acid at the boiling heat on metanitrophenol (A. Bantlin, *Ber.* x. 524).

Methyl-resorcinols (J. Habermann, *Ber.* x. 867). The two methyl-ethers of resorcinol are easily prepared by heating an intimate mixture of 1 mol. of resorcinol, 2 mols. of potassium methylsulphate, and 2 mols. of potassium hydroxide with a little absolute alcohol, for four to five hours, at 160° . The product is acidulated with sulphuric acid, and exhausted with ether, and after the latter has been driven off, the residue is distilled with water, the dimethyl-ether then passing over, while resorcinol and the monomethyl-ether remain behind. The two compounds are extracted by ether, and separated by fractional distillation.

Monomethylresorcinol, $C^6H(OH)(OCH^3)$, is a colourless or pale yellow, very refractive liquid, which is moderately soluble in cold, more freely in hot water and dilute alcohol, and mixes in almost every proportion with absolute alcohol and ether. It has only a faint odour, but its dilute alcoholic solution has an aromatic but not agreeable smell. Its aqueous solution tastes sweetish and burning, and is coloured violet by ferric chloride. Methyl-resorcinol boils at 243° – 244° , and at -17.5° becomes

viscid, but does not crystallise. With alcoholic potash it forms a thick syrupy mass, which turns reddish-brown when exposed to the air.

Dimethyl-resorcinol, $C^6H^4(OCH^3)^2$, is a colourless refractive oil, very much like the monomethyl-derivative, heavier than water, very slightly soluble therein at ordinary temperatures, but dissolving easily at the boiling heat, and very easily in alcohol and ether. It becomes somewhat more viscid at -17.5° , and boils at 214° – 215° . Vapour-density, obs. = 4.7950; calc. 4.7781. Its aqueous solution is not coloured violet by ferric chloride.

Chlorodimethyl-resorcinol, $C^6H^3ClO^2 = C^6H^3Cl(OCH^3)^2$, is produced by passing chlorine gas into a solution of dimethyl-resorcinol in glacial acetic acid, the operation being stopped at the moment when the liquid assumes a deep yellow colour. On leaving the solution to evaporate in a vacuum over quicklime, the monochlorinated compound is obtained in long limpid well-defined needles, which may be purified by filtering, washing with glacial acetic acid, pressure between filter-paper, and recrystallisation from alcohol. This compound melts at 118° , dissolves sparingly in glacial acetic acid and in cold alcohol, easily in ether and in boiling alcohol. **Dichlorodimethyl-resorcinol**, $C^6H^2Cl^2(OCH^3)^2$, produced by the further action of chlorine, is a liquid insoluble in water, somewhat soluble in alcohol, easily soluble in ether and in glacial acetic acid (Hönig, *Ber.* xi. 1039).

Dibromodimethyl-resorcinol, $C^6H^2Br^2(OCH^3)^2$, is obtained by dropping a solution of bromine in glacial acetic acid into dimethyl-resorcinol dissolved in the same acid, till the colour of the bromine-solution no longer disappears. The product, which crystallises out on standing, melts at 137° – 138° , dissolves sparingly in alcohol and glacial acetic acid, easily in ether, and forms transparent shining crystals belonging to the orthorhombic system (Hönig).

Dinitrodimethyl-resorcinol, $C^6H^2(NO^2)^2(OCH^3)^2$, is formed by adding to dimethyl-resorcinol diluted with glacial acetic acid, an equal volume of nitric acid of the ordinary strength. On leaving the solution at rest for about ten minutes and then shaking it with ether, the dinitro-compound dissolves in the ether, and may be purified by evaporating the ether, dissolving the residue in alcohol, and precipitating with water. It forms small red-brown crystals insoluble in water, soluble in alcohol and ether, melting at 67° . **Trinitrodimethyl-resorcinol**, $C^6H(NO^2)^3(OCH^3)^2$, prepared with dimethyl-resorcinol, fuming nitric acid, and strong sulphuric acid, crystallises from alcohol in nearly colourless laminæ melting at 123° – 124° , insoluble in water, easily soluble in alcohol and ether (Hönig).

Aldehydes derived from Resorcinol (Tiemann a. Lewy, *Ber.* x. 2216). These compounds are formed from resorcinol in the same manner as salicylic and paraoxybenzoic aldehydes from phenol, and vanillin from guajacol (pp. 303, 305), namely by the simultaneous action of chloroform and an alkaline hydroxide. The diatomic phenols, however, mostly unite with the aldehydes formed from them, producing colouring matters, much more readily than the monatomic phenols; and to prevent this combination, it is necessary, in preparing aldehydes from these diatomic phenols, to work with more dilute solutions and with a larger excess of alkali and chloroform.

The resorcinol aldehydes are prepared by treating 5 grams of resorcinol with 80 g. sodium hydroxide and 500 to 600 g. water, and then adding 80 g. chloroform, the mixture being heated in a reflux apparatus, gently at first, afterwards more strongly, acidulated with sulphuric acid after all the chloroform has been decomposed, and finally distilled in a current of steam. The distillate then deposits slender needles consisting of

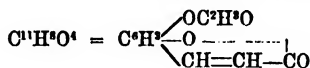
Resorcene-dialdehyde, $C^6H^2(OH)^2(COH)^2$, which dissolves easily in alcohol, ether, benzene, and chloroform, and may be separated from its solution in ether by a solution of acid sodium sulphite. It is nearly insoluble in cold water, crystallises from a large quantity of hot water in thin needles, melts at 127° , and sublimes at 110° . The aqueous solution is coloured red-brown by ferric chloride. The dialdehyde dissolves in alkalis, forming a yellow solution from which it is precipitated by acids. Its ammoniacal solution gives with lead acetate a white precipitate, and with cupric sulphate a green precipitate soluble in ammonia. The alcoholic solution of the dialdehyde, mixed with aniline, immediately deposits needle-shaped crystals melting at 199° . Melting potash converts it into an acid—probably resorcene-dicarboxylic acid—which dissolves easily in water, alcohol, and ether, crystallises from water in white slender needles, and melts at 192° , being resolved at the same time into carbon dioxide and resorcinol.

Resorcyi Aldehyde, $C^6H^4(OH)^2COH$, formed simultaneously with the dialdehyde just described, and remaining in the liquid from which the latter has been

removed by a current of steam, may be extracted from this liquid by ether, after removal of a red amorphous colouring matter—and freed from unaltered resorcinol by combination with acid sodium sulphite, or by recrystallisation from hot benzene. It dissolves readily in water, alcohol, ether, chloroform, and glacial acetic acid, sparingly in benzene, and crystallises from water in yellowish needles melting at 134° – 135° . The aqueous solution is coloured red-brown by ferric chloride. Resoreyl aldehyde is extremely unstable, and is converted by dehydrants or by prolonged exposure to the air into red amorphous bodies. Its conversion by oxidation into an acid of corresponding constitution takes place only after the introduction of ethyl into the hydroxyl-groups.

Diethyl-resoreyl Aldehyde, $C^6H^3(OC^2H^5)^2COH$, is easily formed by the action of ethyl iodide (2 mols.) and KOH (2 mols.) on resorcinol (1 mol.). It crystallises in shining plates, melts at 71° – 72° , dissolves easily in alcohol and ether. By oxidation with potassium permanganate in aqueous solution, it is readily converted into the corresponding acid, $C^6H^3(OC^2H^5)^2COOH$ (diethyl-resoreyl-carboxylic acid), which crystallises in small needles, melts at 99° , and forms well-crystallised slightly soluble salts with barium and calcium. The *lead salt* is a white amorphous precipitate; the *copper salt* a greenish-blue precipitate easily soluble in ammonia.

Resoreyl aldehyde, heated with sodium acetate (1 pt.) and acetic anhydride (3–5 pts.), is converted into a acetoxycoumarin or β -acetumbelliferone:



which crystallises in large faintly yellowish prisms melting at 140° , distils without decomposition, dissolves but sparingly in water even when hot, easily in alcohol and ether. The aqueous solution exhibits a splendid blue fluorescence, but gives no colour-reaction with ferric chloride.

The formation of acetoxycoumarin renders it very probable that at least one of the hydroxyl-groups in resoreyl-aldehyde occupies the *ortho*-position with respect to the COH-group. This compound is not attacked in the cold by alkaline hydroxides or carbonates, but dissolves in them when heated, the solutions after acidulation yielding to ether a substance which, after purification, forms white needles, having the composition of hydroxycoumarin or β -umbelliferone.* $C^6H^3O^3$; sparingly soluble in water (the solution being coloured brown-red by ferric chloride) and decomposing without fusion at 200° .

RESORCINOL-DYES. See RESORCINOL-PHTHALEÏNS, under PHTHALEÏNS (p. 1606).

RESORCINOL-SULPHONIC ACIDS. On the crystalline form of *Potassium Resorcinolmonosulphonate*, $C^6H^4(OH)(OSO^3K)$, see Bodewig (*Zeitschr. f. Kryst. i.* 584; *Jahresh. f. Chem.* 1877, 565).

Resorcinol-disulphonic acid, $C^6H^2S^2O^8 = C^6H^2(OH)^2(SO^3H)^2$, is formed by gradually adding 1 pt. finely pulverised resorcinol to 10 pts. of strong sulphuric acid heated to 150° – 160° , dissolving the crystals which separate by further heating at 190° – 200° , and leaving the solution to cool. The vessel then becomes half filled with large crystals of the disulphonic acid, which may be collected on a suction-filter and washed with strong sulphuric acid. They are colourless, dissolve easily in water and in alcohol, deliquesce on exposure to the air, and are coloured ruby-red by ferric chloride. On boiling the aqueous solution with lime, a *neutral calcium salt* is obtained the solution of which is precipitated on addition of a certain quantity of alkaline carbonate; and on boiling the acid with milk of lime, a *basic salt* is formed, which, like the potassium salt, is too soluble to crystallise well. Barium chloride added to the solution of either of these calcium salts throws down the *barium salt*, $C^6H^2(O^2Ba)(SO^3)^2Ba + 5H^2O$, as a white crystalline precipitate, which does not give off all its water even at 200° . Its formation is analogous to that of the basic phenol-disulphonate of barium, which Städeler obtained (vi. 927) from phenoldisulphonate and carbonate of barium. An aqueous solution of resorcinol-disulphonic acid absorbs a large quantity of *bromine*, producing colourless silky needles of tribromoresorcinol (Piccard a. Humbert, *Ber.* ix. 1479).

Resorcinol-trisulphonic acid, $C^6H(OH)^2(SO^3H)^3$, is formed by heating resorcinol-disulphonic acid with fuming sulphuric acid at 200° . To separate it, the solution is neutralised with milk of lime, whereby an insoluble basic salt is formed,

* The hydroxycoumarin and acetoxycoumarin obtained as above, not having yet been shown to be identical with the umbelliferone and acetumbelliferone previously known (v. 988; vii. 1186), are provisionally distinguished by the prefix β .

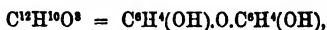
and mixes with the gypsum, whilst any disulphonic acid that may still be present remains dissolved. The liquid is filtered, the residue boiled with hydrochloric acid, and the excess of sulphuric acid precipitated by barium chloride. The strongly acid filtrate, in which the barium resorcinoltrisulphonate remains for a while dissolved, is mixed with ammonia (whereby impurities are precipitated), but not to the point of neutralisation, and then quickly filtered. After a few hours, the clear acid solution begins to deposit the dazzling white crystalline barium salt, the separation of which goes on for two or three days; and a further but less pure salt is deposited on warming. This salt, dried at a very gentle heat, has the composition $[C^6H(OH)_2(SO_3)^3]^{12}Ba^{12} + 3\frac{1}{2}H_2O$. When once deposited, it is no longer soluble in hydrochloric acid. By digesting it at 100° in a sealed tube with ammonium carbonate, ammonium resorcinoltrisulphonate is obtained, which forms, with lead and calcium salts, crystalline precipitates soluble in acetic acid; with barium chloride a precipitate insoluble in acetic acid. With ferric chloride it produces a deep red-violet, very stable coloration (Piccard a. Humbert, *Ber.* x. 55).

RESORCINYL OXIDES or RESORCINOL ETHERS. Boettinger (*Ber.* ix. 182), by treating resorcinol with sodium hydroxide and CO_2 , obtained an acid product consisting mainly of a red substance soluble in alkalis. Barth (*ibid.* 308) obtained the same or a similar substance by treating fused resorcinol with sodium and CO_2 , or with sodium alone,—and in a purer state by the action of hydrochloric acid on resorcinol under pressure. Precipitated from ammoniacal solution by acids, it formed light brown flocks, which when dry exhibited a splendid metallic iridescence, and yielded on trituration a powder having a deep red colour. Heated with zinc dust, it gave off benzene, together with a small quantity of diphenyl formed by a secondary reaction. The compound thus obtained is a dye-stuff imparting a very bright red colour to wool and silk. Barth represents it by the formula $C^{12}H^{10}O^3$, and regards it as a kind of ether of resorcinol. The same substance appears to have been obtained by Barth a. Senhofer (*Liebigs Annalen*, clxiv. 109) by the action of hydriodic acid on diethyl-resorcinol.

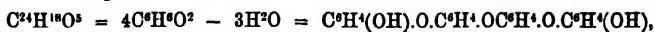
The product of the action of hydrochloric acid on resorcinol has been further examined by Barth a. Weidel (*Ber.* x. 1464), who prepares it by heating 20 grams of resorcinol with 25 c.c. strong hydrochloric acid in a sealed tube at 180° , obtaining thereby an acid liquid, together with a resin which has a green reflex, and when subjected to the following treatment yields two lead salts A and B. The air-dried resin is treated with alcohol of 90 per cent., which dissolves it slowly but almost completely, and the residue may be brought into solution by first dissolving it in ammonia, then precipitating with an acid, and treating the precipitate with alcohol. If now the united alcoholic extracts be mixed with an alcoholic solution of neutral lead acetate, the lead salt A separates out first, and the filtered liquid, freed from alcohol by distillation and mixed with water, yields a mixture of the salts A and B. To separate these, they are dried and warmed with alcohol, which dissolves B and leaves A.

The lead salt A is a violet-red powder from which the lead may be removed either by dissolving it in glacial acetic acid, and precipitating with hydrochloric acid, or by suspending it in alcohol and decomposing it with hydrogen sulphide. In either case, the further purification of the substance freed from lead is effected by mixing the filtrate with water, after expelling the alcohol, dissolving the washed and dried precipitate in ammonia, and reprecipitating with hydrochloric acid.

The compound thus obtained is *resorcinyloxide*,



formed according to the equation $2C^6H^4O^2 = H_2O + C^{12}H^{10}O^3$. After washing and drying, it is a brown-red amorphous powder, acquiring by pressure a green metallic lustre. It melts at a rather high temperature, is nearly insoluble in water, very sparingly soluble in ether and in cold alcohol, moderately soluble in hot alcohol and in glacial acetic acid. It dissolves in strong sulphuric acid without alteration, and in aqueous alkalis, forming a solution having an intense dark red colour and green fluorescence. The *acetyl-derivative*, $(C^6H^4.OC^2H^3O)^2O$, may be prepared by treating the oxide with acetyl chloride at 100° , and purified by precipitation with water, solution in alcohol, and reprecipitation with water. It dissolves in alkalis at ordinary temperatures without alteration, forming a red-violet liquid; with decomposition when heated. The *tetrabromo-derivative*, $C^{12}H^4Br^4O^3 = (C^6H^2Br^2OH)^2O$, is formed by adding bromine in excess to a solution of the oxide in glacial acetic acid, and may be purified by solution in alcohol and reprecipitation with water. Melting potash converts it into resorcinol. When heated with zinc-dust, it does not yield any definite products.

Diresorcinyldioxide,

prepared from the lead salt B by the series of processes above described for A, forms, when dry, a brick-red amorphous powder, melting at a somewhat higher temperature. It dissolves very easily in alcohol, ether, and glacial acetic acid, and is somewhat soluble in water. Aqueous alkalis dissolve it to a brownish-yellow liquid with violet-blue fluorescence. The *acetyl-derivative*, $C^{24}H^{16}(C^2H^3O)^2O^5$, prepared like its analogue above described, is a cinnamon-brown powder becoming strongly electric when rubbed, nearly insoluble in alkalis, very easily soluble in alcohol. The *hexbromo-derivative*, $C^{24}H^{12}Br^6O^5$, prepared as above described, is a light red powder sparingly soluble in alkalis, easily in alcohol and glacial acetic acid. By fusion with potash it yields resorcinol (Barth a. Weidel).

Both of the above-described resorcinyldioxides, when boiled for some time with nitric acid, yield isophthalic acid, a large portion, however, undergoing complete decomposition.

The green fluorescence of monoresorcinyldioxide may serve as a test for the presence of resorcinol. On heating resorcinol with a little hydrochloric acid at 160° – 180° for a few minutes in a sealed tube, then opening the tube, and adding a few drops of ammonia, the green fluorescence will be perceptible even in presence of only $\frac{1}{2}$ mg. of resorcinol (Barth a. Weidel).

RETENE, $C^{18}H^{18}$ (Ekstrand, *Bull. Soc. Chim.* [2], xxiv. 53; *Liebig's Annalen*, clxxv. 75). This hydrocarbon, originally found in scales on fossil pine-stems in beds of peat and lignite (v. 97), occurs also amongst the products of the destructive distillation of wood (vi. 993), and forms a considerable portion of the buttery mass obtained in the latter part of the distillation of wood tar. From this mass it may be obtained in the pure state by pressure at a low temperature, washing with ether, and recrystallisation from alcohol of 95 per cent. with the aid of animal charcoal.

Retene crystallises in white laminae melting at 98.6° . Its sp. gr. in the crystallised state is 1.13; after fusion and resolidification 1.08. Its vapour-density according to W. Knecht (*Ber.* x. 2074), is 8.28 (air = 1); calc. for $C^{18}H^{18}$, 8.1. It has neither taste nor smell. 100 pts. boiling alcohol of 95 per cent. dissolve 69 pts., 100 pts. cold alcohol only 3 pts. of retene. Glacial acetic acid dissolves it readily with the aid of heat, and deposits the greater part of it on cooling. It dissolves easily in ligroin, carbon sulphide, benzene, and ether, but is insoluble in water. With chlorine and bromine at ordinary temperatures it forms addition-products which decompose when heated, yielding products of substitution. Retene is but very slightly attacked by nitric acid at ordinary temperatures, more easily when heated; fuming nitric acid dissolves it at ordinary temperatures, and water added to the solution throws down a yellow precipitate, the solution of which in alcohol or acetic acid leaves resinous products on evaporation.

A compound of retene with *dinitroanthraquinone* is obtained by evaporating a solution of the two bodies in glacial acetic acid, and crystallises in small needles of a dark orange-red colour.

Retene-picric acid, $C^{18}H^{18}.C^6H^2(NO^2)^2OH$, crystallises from alcoholic solution in orange-yellow needles, melts at 123° , dissolves in 5 pts. boiling alcohol of 95 per cent. in 44 pts. alcohol at 10° , and is decomposed by water.

Sodium-amalgam does not appear to act upon retene in alcoholic solution. Retene also remains for the most part unattacked when heated with hydriodic acid (sp. gr. 1.68) and red phosphorus at 175° – 200° ; combustible gases are, however, formed, probably hydrocarbons of the fatty series. When retene is passed in vapour over heated lead oxide, a considerable portion of it remains unaltered, a small quantity of naphthalene being, however, produced, together with water.

Chlororetene, $C^{18}H^{17}Cl$. When retene is exposed for a month to the action of chlorine at ordinary temperatures, a greenish viscid fuming mass is formed, which melts without dissolving when treated with boiling alcohol; and on digesting this product with alcoholic potash, then washing it with water, dissolving it in ether, and leaving the ether to evaporate, chlororetene separates as a red syrupy substance which decomposes when heated, with carbonisation and evolution of chlorine.

Bromoretene. When retene is exposed to the action of bromine-vapour, and the product is treated with alcoholic potash, then dissolved in ether, and left to evaporate, a brownish syrup is obtained, containing 34.4 to 34.6 per cent. bromine [intermediate between mono- and di-bromoretene].

Dibromoretene, $C^{18}H^{16}Br^2$, is prepared by heating 1 mol. retene on the water-bath with 2 mols. bromine and water, washing the product with warm dilute potash-ley and with alcohol, treating the grey viscid mass with alcoholic potash, washing it

repeatedly with water and alcohol, then digesting it with ether and crystallising the white powder which remains undissolved from carbon sulphide. It crystallises in colourless plates, melts at 180° , dissolves readily in carbon sulphide and in ligroin, but is nearly insoluble in ether.

Tetrabromoretene, $C^{10}H^{14}Br^4O^4$, is obtained by acting on retene with excess of bromine, treating the product with boiling aqueous potash and with ether, and re-crystallising the residue from carbon sulphide. It forms colourless prisms, melts at 110° – 112° , is insoluble in alcohol, slightly soluble in acetic acid and in ether, more easily in ligroin, very easily in boiling benzene and carbon sulphide.

When 1 mol. retene is heated in a sealed tube placed in a water-bath with 5 mols. bromine, the product treated with potash ley, water, and alcohol, and then boiled with ether, the tetrabromoretene just described remains undissolved, and the ethereal solution when left to evaporate leaves a compound isomeric therewith, in the form of a resinous mass, slightly soluble in ether and in ligroin, very soluble in carbon sulphide. This modification of tetrabromoretene is also formed from the tetrabromide of dibromoretene, $C^{10}H^{16}Br^2$, by the action of alcoholic potash.

Oxidation-products of Retene. When warm solutions of retene and chromic acid in glacial acetic acid are mixed together, a violent action takes place, the liquid on cooling becoming filled with needle-shaped crystals; and on diluting with water, and treating the residue with solution of sodium carbonate, and then with warm ether, which removes a viscid mass, the chief product, $C^{10}H^{14}O^2$ (called dioxystetistene by Wahlfors, vi. 994) remains undissolved. The soda-solution with which the crude product has been treated, yields, when concentrated, yellow scaly crystals the solution of which gives a flocculent precipitate with sulphuric acid. On treating this precipitate with alcohol at 50° , a brown mass remains undissolved, and the liquid on cooling deposits yellowish shining scales. By saturating the mother-liquor of the first-separated scales with sulphuric acid, a brown precipitate is formed which when boiled with water partly dissolves, forming a yellow liquid, from which hydrochloric acid throws down white nearly insoluble flocks; and from this precipitate alcohol extracts the compound $C^{10}H^{16}O^2$, which crystallises in yellow shining scales. When the residue left after the extraction of this last compound is boiled for some time with concentrated baryta-water, a brown-yellow solution is obtained, yielding, on addition of hydrochloric acid, a brown precipitate from which, by repeated crystallisation from boiling alcohol, the compound $C^{10}H^{17}O^2$ is obtained in colourless needles.

Dioxystetistene crystallises on cooling from its hot alcoholic solution in flat, deep orange-coloured prisms, melts at 190° , sublimes in orange-red needles without decomposition when cautiously heated, and is moderately soluble in benzene and acetic acid. 100 pts. boiling alcohol of 95 per cent. dissolve 2.2 to 2.3 pts. of it; cold alcohol only 0.15 pts. It is not attacked by chlorine at ordinary temperatures, but bromine acts upon it, with elimination of hydrogen. When heated with ordinary nitric acid, it dissolves unaltered, but the fuming acid converts it into a nitro-product. Sulphuric acid dissolves it without alteration, but on heating it with the acid on the water-bath, sulphur dioxide is evolved, and on cooling, a red gelatinous mass is formed, which gives red crystalline flocks when boiled with water. By prolonged boiling with chromic acid in acetic acid solution it yields oxidation-products soluble in aqueous sodium carbonate. It is not altered by dilute solution of potassium or sodium hydroxide, but the concentrated alkalis convert it into a greenish resinous mass. When fused with potassium hydroxide, it yields a black mass, forming with water a red solution which yields with sulphuric acid a greenish precipitate consisting of a mixture of several bodies, from which ether extracts a red viscid mass, while the residue dissolves in carbon sulphide or in benzene with a fine blue or greenish-blue colour. Dioxystetistene dissolves with difficulty in solution of acid sodium sulphite, and is precipitated therefrom by hydrochloric acid in its original state.

The compound called by Wahlfors '*monobromoretistene*,' obtained by the action of 2 mols. bromine on 1 mol. dioxystetistene, has, according to Ekstrand, the empirical formula $C^{10}H^{11}BrO^2$. It crystallises from glacial acetic acid in small red prisms, melts at 234° – 235° , is slightly soluble in alcohol, ether, and carbon sulphide, more soluble in benzene and glacial acetic acid.

When dioxystetistene is heated with 10 pts. baryta, there is formed, together with water and combustible gas, a red oil which solidifies after some time, and yields to boiling alcohol a body, $C^{10}H^{21}O$, which crystallises in long flat colourless needles, melts at 89° – 90° , and is insoluble in aqueous sodium carbonate. The residual oil yields by fractional distillation a liquid which has the composition $C^{10}H^{22}$, and boils at 215° – 220° .

Dioxystetistene is not altered by the action of sulphurous acid in alcoholic solution, but when heated with zinc-dust and potash-ley it partly dissolves, and the solution

yields with hydrochloric acid a green precipitate of a quinol, which on exposure to the air is quickly reoxidised to dioxyretistene. Dioxyretistene, distilled with zinc-dust, yields, together with retene, a small quantity of a hydrocarbon, $C^{14}H^{14}$, which melts at 56° – 57° , and is probably dibenzyl.

The compound $C^{18}H^{16}O^2$ (p. 1755) crystallises in colourless shining scales, melts at 139° , dissolves very easily in alcohol, ether, and glacial acetic acid, sparingly in water, from which it crystallises in shining scales; the solution has an acid reaction. The sodium salt, $C^{18}H^{16}NaO^2$, crystallises in shining scales; the potassium salt likewise. The barium salt, $(C^{18}H^{16}O^2)_2Ba$, forms large colourless laminæ. The solution of the sodium salt forms with ferric chloride, after a while, a precipitate consisting of small needles; with lead acetate, a bulky precipitate becoming crystalline after some time; with silver nitrate a precipitate made up of microscopic prisms.

The compound $C^{18}H^{16}O^2$ (p. 1755) melts at 222° , may be sublimed, and dissolves easily in alcohol, ether, and glacial acetic acid. The sodium salt, $C^{18}H^{16}NaO^2$, forms large brown-yellow laminæ, and dissolves with moderate facility, its solution giving amorphous precipitates with lead acetate and silver nitrate. The barium salt forms small shining scales.

RETENESULPHONIC ACIDS (Ekstrand, *Liebig's Annalen*, clxxxv. 86).

Retenedisulphonic acid, $C^{18}H^{16}(SO^2H)^2$.—When retene is gradually added to a mixture of equal volumes of concentrated and fuming sulphuric acid, and the liquid is left to itself for two to three weeks, slender needles of the compound $C^{18}H^{16}(SO^2H)^2 + 5H^2SO^4$ separate out. The free disulphonic acid obtained from the barium or lead salt is very soluble, and separates from a concentrated aqueous solution in small needles and from glacial acetic acid in well-defined needles or prisms. Its concentrated aqueous solution is precipitated by sulphuric acid; and the compound thus formed seems to contain varying quantities of the latter acid. The following salts have been prepared and analysed:

$C^{18}H^{16}(SO^2K)^2$	+	$\frac{1}{2}H^2O$ (at 100°),	silky needles,	in 5–6	1 part dissolves of water
$C^{18}H^{16}(SO^2Na)^2$	+	$\frac{1}{2}H^2O$	" "	in 2–3	"
$C^{18}H^{16}(SO^2Ba)^2$	+	H^2O	prisms, slowly	in 60–61	"
$C^{18}H^{16}(SO^2Sr)^2$	+	$1\frac{1}{2}H^2O$ (at 100°)	"	in 24–25	"
$C^{18}H^{16}(SO^2Ca)^2$	+	$1\frac{1}{2}H^2O$	"	in 20–21	"
$C^{18}H^{16}(SO^2Mg)^2$	+	$2H^2O$ (at 100°),	woolly needles,	in 25–26	"
$C^{18}H^{16}(SO^2Cu)^2$	+	$1\frac{1}{2}H^2O$	" pale green	in 3–4	"
$C^{18}H^{16}(SO^2Pb)^2$	+	$5H^2O$ (at 15°),	long needles		"
		H^2O (at 100°),	long prisms,		
			slowly in 54–55		"

Retenedisulphonic dichloride, $C^{18}H^{16}(SO^2Cl)^2$, obtained by the action of phosphorus pentachloride on the potassium salt, crystallises from hot glacial acetic acid in hard prisms, melting at 175° ; it dissolves readily in benzene, sparingly in ether, and is scarcely attacked by boiling water, which does not decompose it completely till the temperature is raised to 160° .

An isomeric retenedisulphonic acid appears to exist.

Retenetrisulphonic acid, $C^{18}H^{16}(SO^2H)^3$, is formed by heating retene with a mixture of common and fuming sulphuric acid on a water-bath; it is readily soluble in water; is not precipitated by sulphuric acid; and is obtained on cooling from a very concentrated aqueous solution as a crystalline mass, which dissolves very readily in water, alcohol, and acetic acid. Its barium salt, $[C^{18}H^{16}(SO^2Ba)]^3 + \begin{cases} 3H^2O \text{ at } 100^{\circ} \\ 18H^2O \text{ at } 15^{\circ} \end{cases}$ differs somewhat in form and solubility according to the manner in which it is prepared (crystallising in needles soluble in 16 pts. water, or in prisms soluble in 11 pts.) The lead salt, $[C^{18}H^{16}(SO^2Pb)]^3 + \begin{cases} 3H^2O \text{ at } 100^{\circ} \\ 18H^2O \text{ at } 15^{\circ} \end{cases}$ forms thin needles.

The acid obtained by treating retene with sulphuric anhydride yields three different barium salts.

REZBANYITE. See COSALITE (p. 572).

RHABDOPHANE. This name has been given to a very rare mineral from Cornwall, consisting essentially of didymium and erbium phosphates (Lettsom, *Compt. rend.* lxxvi. 1028).

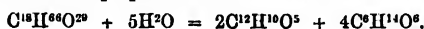
RHAGITE. A bismuth arsenate, $5Bi^2O^3, 2As^2O^5 + 8H^2O$, sp. gr. 6.82, occurring together with several uranic arsenates (vii. 1190), in the White Hart Mine, near

Schneeberg in Saxony. Its analysis by C. Winckler (*Jahrb. Min.* 1871, 869; 1874, 682) gave:

Bi ² O ³	As ² O ³	H ² O	Fe ² O ³ , Al ² O ³	CoO	CaO	Matrix
72.8	14.2	4.6	1.6	1.5	0.5	3.3 = 98.5

RHAMNUS. The glucoside of yellow berries (*Rh. infectorius*), called xanthorhamnin by Gellatly, rhamnegin by Schützenberger, and its derivatives, have been examined by Liebermann a. Hörmann (*Ber.* xi. 952, 1618), with results different from those obtained by previous investigators (v. 100; vi. 994; vii. 561).

Xanthorhamnin, boiled with dilute sulphuric acid, readily splits up into rhamnetin, C¹²H¹⁰O⁵, and a sugar, supposed by Liebermann a. Hörmann to be different from all others yet known, and named by them 'rhamnodulcite.' Behrend, however (*Ber.* xi. 1353), has shown that it is identical with isodulcitol, C⁶H¹⁴O⁶ (p. 1131). Xanthorhamnin is also converted into rhamnetin by simply heating it at 130°–160°. Liebermann a. Hörmann assign to xanthorhamnin the formula C⁴²H⁶⁶O²², which agrees nearly with the analysis of the potassium-derivative (*infra*), and represents correctly the resolution of xanthorhamnin into rhamnetin and isodulcitol, these products being formed in the proportion of 1 mol. rhamnetin to 2 mols. dulcitol:



Potassium-xanthorhamnin, C⁴⁸H⁸²K⁴O²², is obtained on mixing an alcoholic solution of xanthorhamnin with a slight excess of alcoholic potash, as a thick yellow precipitate which, after rapid filtration, washing with alcohol, and drying over sulphuric acid, forms a yellow powder, yielding by analysis 11.81 per cent. potassium; calc. 12.40 per cent. It is tolerably permanent when dry, but becomes brown and resinous when moist.

Rhamnetin, C¹²H¹⁰O⁵, crystallises from water containing sulphuric acid in microscopic needles; from phenol in distinct yellow needles.

Dibromorhamnetin, C¹²H⁸Br²O⁵, prepared by adding bromine to finely pulverised rhamnetin suspended in glacial acetic acid, forms beautiful yellow needles, easily soluble in hot alcohol and hot glacial acetic acid, also in benzene; alkalis dissolve it with yellow colour. It dyes like rhamnetin, only with a somewhat redder tint.

Diacetyl-rhamnetin, C¹²H⁸(OC²H³O)²O⁵, is obtained by boiling rhamnetin with acetic anhydride and anhydrous sodium acetate in a vessel with upright condenser, till a portion of the crystallised product is no longer coloured by dilute alkali. It crystallises from alcohol containing one-tenth part of acetic anhydride in white silky needles melting at 185°.

Dibromoacetyl-rhamnetin, prepared in like manner from dibromorhamnetin, forms white shining needles which turn yellow at 200°, and melt at 211°–212°.

Dipropionyl-rhamnetin, C¹²H⁸(OC³H³O)²O⁵, prepared like the acetyl-compound with sodium propionate and propionic anhydride, crystallises in light yellow needles melting at 158°–162°.

Dibenzoyl-rhamnetin, C¹²H⁸(OC⁷H⁵O)²O⁵, prepared by heating 1 pt. rhamnetin with 4 pts. benzoic anhydride at 150°, crystallises in small silky almost colourless needles, easily soluble in glacial acetic acid, sparingly in chloroform and in alcohol, melting at 210°–212°.

Dimethyl-rhamnetin, C¹²H⁸(CH³)²O⁵, is formed by heating xanthorhamnin at 120°–130°, with potassium methyl-sulphate and absolute methyl alcohol, the xanthorhamnin being first converted, with separation of isodulcitol, into rhamnetin, which then takes up 2 at. methyl. Dimethyl-rhamnetin crystallises in needles having a very faint yellowish tint, and melting at 156°–157°.

RHODIUM. Pulverised rhodium decomposes formic acid, with rise of temperature, into water and carbon dioxide. When the decomposing power slackens, it may be restored by washing the metal and drying it in the air. Alcohol is also decomposed by rhodium in presence of alkalis, at a temperature only a little above that of the air, hydrogen being given off, and an alkaline acetate produced. The same action is produced by iridium, but not by platinum or palladium (Deville a. Debray, *Compt. rend.* lxxviii. 1782).

On *Mercaptide of Rhodium*, see p. 1276.

RECADINE. On the occurrence of this base in the unripe capsules of the red poppy (*Papaver Rhæas*), see p. 1664.

RHUBARB. From a comparison of observations made in the last few years on the sources of officinal rhubarb, H. Werner (*Arch. Pharm.* [3], xi. 116) concludes that Russian and Chinese rhubarb are obtained from *Rheum palmatum*, and that this plant

is indigenous in the Upper Hoang-ho in the Highland of West China around Lake Koko-nur.

Comparative analyses of different kinds of rhubarb have been made by Dragendorff (*Pharm. J. Trans.* [3], viii. 826):

I. *Rheum Moscovicum*, imported in 1860 with the last consignment of the Crown rhubarb.

II. *Rheum Chinense*, delivered from the Crown Warehouse, St. Petersburg, 1877.

III. *Rheum palmatum Tanguticum*.

IV. *Rheum anglicum cultum* from Moscow.

V. Rhubarb cultivated in Siberia.

	I	II	III	IV	V
Moisture	9.52	11.25	10.35	11.09	8.69
Ash	8.27	6.32	24.05	3.20	10.38
Mucilage soluble in water	3.35	1.58	1.71	2.55	3.08
Arabic acid soluble in water not precipitated by alcohol	5.82	6.43	3.17	8.32	2.01
Metarabic acid	3.82	5.70	2.57	3.22	8.47
Pararabin	3.91	2.10	3.54	1.95	3.02
Starch	8.40	6.20	6.32	16.50	11.95
Cellulose	7.45	7.64	4.91	4.29	8.61
Sugar	5.55	4.29	3.94	4.40	3.66
Substance readily soluble in absolute alcohol, probably a carbohydrate	2.70	6.47	7.41	8.21	1.95
Cathartic acid	5.25	4.88	2.03	2.50	2.26
Malic acid, &c.	0.04	1.09	trace	0.17	1.24
Calcium oxalate	3.28	4.59	4.19	1.12	2.15
Chrysophanic acid soluble in petroleum spirit	—	trace	trace	trace	1.01
Chrysophane and tannin	17.13	14.17	8.22	4.83	7.84
Emodin, erythreoretin, phæoretin, &c.	1.13	1.15	1.18	5.89	6.29
Dark brown crystalline resin, &c., soluble in alcohol and ether	1.00				
White crystalline resin soluble in ether, insoluble in alcohol	0.15	0.70	0.49	2.32	2.75
Fat	0.05	0.15	0.32	6.17	trace
Albuminoid substances	4.37	4.39	4.33	3.17	3.92
Paracellulose, vasculose, pectose, lignin, &c.	18.81	10.90	8.68	16.10	10.72

Cathartic acid appears to be the purgative, and tannin and chrysophane the tonic constituents of rhubarb, so that No. I. and II. must be regarded as best adapted for therapeutic purposes.

On the detection of Turmeric in Rhubarb, see TURMERIC.

RICINOLEIC ACID, $C^{18}H^{34}O_2$. This acid may be purified by fractional precipitation of crude castor-oil soap with calcium chloride. If the first fractions, amounting to about a third of the entire precipitation, be rejected, the following $\frac{2}{3}$ will be found to consist of pure calcium ricinole (Claus a. Hilkenkamp, *Ber.* ix. 1916).

Hydriodic acid appears to act but slightly on ricinoleic acid at 100° – 170° ; but on gradually adding phosphorus and iodine to a warm emulsion of ricinoleic acid in a small quantity of water, a yellow oil is obtained, consisting of iodostearidenic acid, $C^{18}H^{32}IO_2$. This acid easily takes up 1 mol. bromine, forming the acid $C^{18}H^{32}Br^2IO_2$, and when treated with nascent hydrogen (zinc-filings and dilute hydrochloric acid) it is converted into stearic acid (Claus a. Hilkenkamp).

RICINUS. The leaves of the castor-oil plant (*Ricinus communis*) have been examined by E. S. Wayne (*Pharm. J. Trans.* [3], iv. 749), who finds in them ricinine and considerable quantities of potassium nitrate. They yielded 24 per cent. ash containing:

CaO	MgO	K ² O	Na ² O	Fe ² O ³	P ² O ⁵	SO ³	Cl	CO ²	Silica and sand	Loss	
33.40	6.20	27.15	2.12	0.70	6.68	2.90	1.63	16.20	2.41	0.61	= 100

When castor-oil is distilled under reduced pressure, a colourless oil, amounting to about a third of its volume, passes over, together with a small quantity of a watery liquid, while a spongy saponifiable mass remains in the retort. The oily distillate consists, to about one-half, of cenanthaldehyde, and, after this has passed over, the thermometer suddenly rises considerably, then remains stationary for some time, and a body collects in the receiver, which solidifies to a crystalline mass, and appears to be a new acid of the oleic series. It melts at 24.5° , boils at 198° – 200° , under a pressure of 90 mm., and gives by analysis numbers agreeing with the formula $C^{11}H^{20}O^2$. It is resolved by fusion with potash into acetic and nonoic acid, $(C^8H^{18}O^2)$, and yields with bromine an addition-product, from which hydrobromic acid is readily extracted by alcoholic potash (F. Krafft, *Ber.* x. 2034).

RIPIDOLITE. This mineral from the Zillerthal has been analysed by A. J. Egger (*Min. Mitth.* 1874, 244), with the following results:

SiO ²	Al ² O ³	Fe ² O ³	FeO	CaO	MgO	H ² O	Sp. gr.
26.02	20.16	1.07	28.08	0.44	15.50	9.65 = 100.92	2.955

RIVOTITE. An amorphous mineral of yellow-green to dark grey-green colour, occurring, contaminated with malachite and imbedded in limestone, on the western declivity of the Sierra del Cadi, in the province of Lerida in Spain. It has been analysed by X. Ducloux (*Compt. rend.* lxxviii. 1471), who represents the results by the formula $Sb^2O^3 + 4(Cu,Ag)CO^2$:

Sb ² O ³	CO ²	CuO	Ag ² O	CaO	Sp. gr.
42.00	21.00	39.50	1.18	trace = 103.68	3.55–3.62

ROCELLA FUCIFORMIS. This lichen, which is characterised by an intensely bitter taste, has been examined by Stenhouse & Groves (*Proc. Roy. Soc.* xxv. 60). It was treated with milk of lime, dried and exhausted with hot alcohol; the extracts were freed from alcohol; the residue was boiled several times with small quantities of alcohol, and then with benzene to remove fat and chlorophyll; and the residue then left was dissolved in boiling alcohol and filtered hot. The alcoholic solution on cooling deposited two kinds of crystals—slender feathery crystals of a substance which has not yet been examined, and large shining prisms of a substance having the composition $C^{27}H^{29}N^3O^2$, designated as *Picrorocellin*. This compound melts at 192° – 194° , is moderately soluble in hot alcohol, sparingly in ether and in benzene, nearly insoluble in water, petroleum, and carbon sulphide. By oxidation with chromic acid mixture it yields benzaldehyde and benzoic acid.

Xanthorocellin, $C^{21}H^{17}N^2O^2$, is formed by heating picrorocellin to 220° , or boiling it with dilute hydrochloric or sulphuric acid, or best by dissolving it in acetic acid, and boiling the solution, after adding a few drops of hydrochloric acid. It crystallises in yellow needles, dissolves easily in hot alcohol, and is strongly attacked by hot nitric acid, yielding a substance not yet analysed, which crystallises in hexagonal prisms.

Picrorocellin, boiled with aqueous or alcoholic soda-ley, yields a substance which crystallises in large colourless prisms, melts at 154° , and gives by analysis numbers agreeing nearly with the empirical formula $C^{24}H^{25}N^2O^2$.

ROGERSITE. See NIOBATES (p. 1395).

ROMAN CHAMOMILE OIL. The acid product obtained by saponifying this oil—hitherto regarded as a single acid, viz. angelic acid (p. 86)—is now found to be a mixture of two isomeric bodies, $C^8H^8O^2$, viz. angelic acid, melting at 45° – 45.5° , and boiling at 185° (not at 194° as formerly stated), and tiglic acid, melting at 64.5° and boiling at 198.5° , together with small quantities of isobutyric acid, and a fourth acid, not yet isolated, but probably consisting of methacrylic acid (Fittig & Kopp, *Ber.* ix. 1195).

Koebig (*Liebigs Annalen*, xcxcv. 92), by submitting the oil to careful fractional distillation, has shown that it consists of a mixture of isobutylic isobutyrate, isobutylic angelate, amylic angelate, and amylic tiglate, together with the angelic and tiglic ethers of a new primary hexyl alcohol (sp. gr. 0.8295 at 15° , b. p. 152 – 153°), and the corresponding ethers of terpene-alcohol or anthemol. Other substances, if present at all, can exist in the oil only in very small quantities.

ROSANILINE, $C^{20}H^{19}N^3$. This base is formed by digesting aurin with alcoholic ammonia at 150° for several days, or with aqueous ammonia at 120° for twenty hours; if the action be longer continued, leucaniline is produced. At 180° the reaction proceeds more quickly, with formation of rosaniline (Dale & Schorlemmer, *Ber.* x. 1016, 1128), see AURIN (p. 136). According to Monnet, Reverdin & Nölting (*Ber.* xii. 445),

the presence of meta-toluidine in commercial toluidine from which rosaniline is prepared, injures the purity of the colours.

Rosenstiehl (*Compt. rend.* lxxxii. 415; *Ann. Chim. Phys.* [5], viii. 176; *Chem. Soc. J.* xxix. 935) describes three isomeric rosanilines obtained: (a) from aniline and paratoluidine; (β) from ortho-toluidine (pseudotoluidine) alone, or from ortho-toluidine and aniline; (γ) from ortho- and para-toluidines, or from a mixture of these two bases with aniline. This modification forms the chief constituent of toluidine-red and of the fuchsines. As β-roosaniline is formed from o-toluidine alone, the latter must first be partly converted by the oxidising agent into aniline. All the three rosanilines are resolved into their components by the action of hydriodic acid.

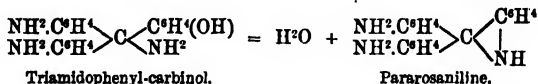
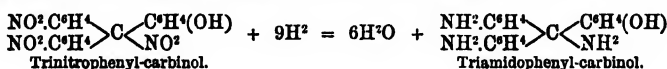
Diazorosaniline is formed from rosaniline by the action of nitrous acid. Its *aurochloride*, $C^{20}H^{13}N^4Cl^3 \cdot H^2O + AuCl^3$, is a light yellow flocculent crystalline precipitate, which detonates when heated, and when boiled with water gives off all its nitrogen in the free state. The *platinochloride*, $(C^{20}H^{13}N^4Cl^3 \cdot H^2O)^2 \cdot 3PtCl^4 + 6H^2O$, likewise gives off all its nitrogen when boiled with water, leaving a residue containing rosolic acid. The *aurochloride* of diazohydrocyanorosaniline, $C^{20}H^{14}(CN)N^4Cl^3 \cdot 3AuCl^3$, is a yellow flocculent precipitate, which, when boiled with water, gives off only 6 atms. nitrogen. The *sulphate* is decomposed by boiling water, yielding hydrocyanorosolic acid (E. a. O. Fischer, *Liebig's Annalen*, exciv. 277).

Diazo-leucaniline is formed by passing nitrous gas into leucaniline hydrochloride. Its *hydrochloride* is a light yellow sticky mass, forming with auric chloride the sparingly soluble double salt, $C^{20}H^{13}N^4Cl^3 \cdot 3AuCl^3 + H^2O$.

When leucaniline is dissolved in strong sulphuric acid, the solution in small portions treated with nitrous acid, and the resulting red liquid added, with stirring, to boiling alcohol, a dark red liquid is obtained, which when neutralised deposits an oil yielding on distillation tolyldiphenylmethane, $C^{20}H^{18} = CH(C^6H^5)(C^6H^5)^2$. Hence it appears that diazo-leucaniline is converted by boiling alcohol into tolyldiphenylmethane (E. a. O. Fischer).

Pararosaniline, $C^{19}H^{17}N^3 = \frac{NH^2 \cdot C^6H^4}{NH^2 \cdot C^6H^4} > C < \frac{C^6H^4}{NH}$ (E. a. O. Fischer, *Ber.* xi.

195, 473, 612, 1079, 1598; *Liebig's Annalen*, exciv. 242). This base is formed: 1. By oxidising a solution of trinitrotriphenylmethane, $C^{19}H^{12}(NO^2)^3$, in glacial acetic acid with chromic acid, whereby it is converted into trinitro-triphenyl carbinol, $C^{19}H^{12}(NO^2)^3OH$, and reducing the latter with zinc-dust, taking care that the action does not go too far, as otherwise paraleucaniline will be formed. The transformation takes place by two stages, as represented by the following equations:

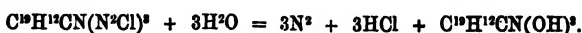


Diazopararosaniline, produced by the action of nitrous acid on pararosaniline, forms a hydrochloride:



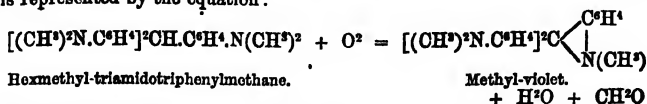
which is decomposed by boiling with water, with formation of aurin or pararosolic acid, $C^{19}H^{14}O^2$. It unites with auric chloride, forming a yellow crystalline double salt slightly soluble in water.

Hydrocyanopararosaniline, $C^{20}H^{15}N^4 = C^{19}H^{17}N^3 \cdot CNH$, easily obtained by direct combination, crystallises from hot alcohol, in which it is but slightly soluble, in colourless oblique prisms. Its hydrochloride decomposes at 180°–190° into HCl, HCN, and parafuchsine. Nitrous acid converts the base into diazohydrocyanopararosaniline, the hydrochloride of which, $C^{20}H^{15}N^4Cl^3 + 2H^2O$, forms slender, colourless, very explosive needles, and is decomposed by boiling with water, yielding a compound identical with the hydrocyano-derivative which Graebe a. Caro obtained from aurin:



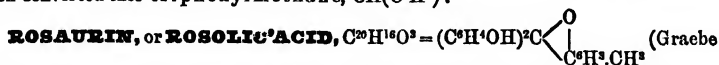
Pentamethyl-pararosaniline, $C^{19}H^{14}(CH^3)^5N^3$.—This, according to E. and O. Fischer (*Ber.* xi. 2095), is the constitution of methyl-violet, which is produced by

the oxidising action of manganese dioxide and sulphuric acid on hexmethyl-triamidotriphenyl-methane, the product of the action of 1 mol. chloral on 3 mols. dimethylaniline in presence of zinc chloride. The formation of methyl-violet from this hexmethylated base is represented by the equation:



Paraleucaniline, $\text{C}^{10}\text{H}^{10}\text{N}^3$, is produced by the action of nascent hydrogen (Zn and HCl) on pararosaniline, and is precipitated as a hydrochloride, $\text{C}^{10}\text{H}^{10}\text{N}^3.3\text{HCl} + \text{H}_2\text{O}$. The free base may be obtained by adding zinc-dust to a solution of trinitrotriphenylmethane or trinitrotriphenylcarbinol in glacial acetic acid till the red colour disappears. It is precipitated by ammonia, and converted into pararosaniline by oxidising agents, most readily by heating the free base for a short time with a syrupy solution of arsenic acid at 130° – 140° . *Paraleucaniline hydrochloride*, heated at 150° – 160° , is partly converted into fuchsine.

Paraleucaniline is converted by nitrous acid into a diazo-compound, the hydrochloride of which, $\text{C}^{10}\text{H}^{10}\text{ON}^+\text{Cl}^-$, crystallises with difficulty, and imparts a greenish-blue colour to solutions. By dissolving paraleucaniline in strong sulphuric acid, treating the solution by small portions with nitrous acid, and proceeding in the manner already described for leucaniline (p. 1760), diazoparaleucaniline is first produced, and then converted into triphenylmethane, $\text{CH}(\text{C}_6\text{H}_5)^3$.



a. Caro, *Ber.* vi. 1390; *Liebig's Annalen*, clxx. 184; Dale a. Schorlemmer, *Ber.* x. 2230; *Chem. Soc. J.* xxxv. 159). This compound is formed by the action of nitrous acid on rosaniline:



It was formerly supposed to be produced by the action of oxalic acid on phenol in presence of sulphuric acid; but Dale a. Schorlemmer have shown that the product of this reaction is not rosaurin, but its lower homologue, aurin, $\text{C}^{18}\text{H}^{14}\text{O}^3$ (p. 1763). At present the reaction above mentioned is the only one by which rosaurin has been obtained. The name 'rosaurin' is proposed by Dale a. Schorlemmer in preference to the older name, rosolic acid, to indicate the homology of the compound to aurin, and the resemblance which it exhibits to aurin in its power of combining with acids.

Preparation.—500 grams of rosaniline (or the corresponding quantity of a rosaniline salt) are dissolved in a mixture of 1500 c.c. of concentrated hydrochloric acid with 1500 c.c. of water, and the brownish-yellow liquid which is formed is diluted, after filtration, with about 150 litres of cold water. A dilute solution of sodium or potassium nitrite is gradually added, with constant stirring, till the rosaniline has almost but not quite disappeared. This point may be determined by placing from time to time a drop or two of the mixture on filter paper, and watching the outside part of the circle formed. As long as rosaniline is present, a red border is produced, and the addition of the nitrite must be continued till this appears very faint, but still perceptible. The liquid is then gradually heated to boiling, and as soon as the evolution of gas ceases, it is quickly filtered. On cooling, tolerably pure rosaurin separates in fine, brilliant, brownish green crystals. To purify this product, it is dissolved in caustic soda, and the solution is saturated with sulphurous acid. The impurities separate in dark brownish-red flocks, and by addition of a mineral acid to the nearly colourless liquid and gentle warming, the rosaurin is obtained in a state of great purity. Obstinately adhering inorganic salts are best got rid of by solution in alcohol and precipitation with hot water. The best way to crystallise rosaurin is from dilute alcohol, or by decomposing a hot saturated alcoholic solution with boiling water. In the first case, ruby-red crystals are slowly formed, while in the second greenish plates with metallic lustre separate out.

Rosaurin dissolves very easily in hot alcohol, somewhat more sparingly in the cold, and is also moderately soluble in glacial acetic acid and ether, but insoluble in benzene and carbon disulphide. Water dissolves it slightly, acids a little more freely. These solutions have a yellowish-red colour. Rosaurin dissolves in alkalis with a red colour, which in thin layers becomes of a bluish-red, in thick layers of a yellowish-red tint. In accordance with this the absorption spectrum in a somewhat deep-coloured solution consists only of a bright band (from 30 to 50 on the scale of the Kirchhoff-Bunsen apparatus). On dilution a violet streak appears; on still further dilution the bright streaks extend, and finally only a broad dark band is seen,

the middle of which is situated at 64 to 65, but at 95 the green is very feeble. Rosaurin does not melt when heated to 270° . On stronger heating a bulky carbonaceous mass is formed, and phenol and water escape.

Reactions.—Rosaurin has but a very feeble acid character, and therefore does not easily form well-characterised salts with bases. The ammonia salt separates in the form of steel-blue needles, and dissolves with difficulty in alcohol, but easily in water. It gradually loses its ammonia on exposure to air as well as by washing. The barium and lead compounds also decompose when washed. *Reducing agents* convert rosaurin into hydrosaurin. A solution of a rosaurin-compound in caustic soda is easily decolorised by warming with zinc-dust. Sodium-amalgam produces the same result. On the other hand, sulphurous acid does not effect this reduction even at 200° . Rosaurin dissolves, with the aid of heat, in *potassium cyanide*, and acids added to the colourless solution throw down hydrocyanorosaurin. *Acid sulphites of the alkalis* dissolve and perfectly decolorise rosaurin, and thus afford a test of its purity.

Oxidising agents act readily on rosaurin, giving rise to compounds which dissolve in alkalis, with formation of the same colour as the acid, and are precipitated of a vermilion colour, but are difficult to crystallise. In such cases a compound containing more oxygen, and answering to the formula $C^{20}H^{14}O^3$, seems to be formed.

When rosaurin is heated with *water* at 220° – 250° , a colourless body easily soluble in water is formed, in addition to brownish products of decomposition and phenolic bodies. This colourless compound may be obtained free from admixture, by extraction with boiling water, evaporation, and repeated crystallisation. In its properties and the result of its analysis it agrees with the compound which Liebermann obtained by heating rosaniline with water at 270° . It melts at about 200° , and has a composition which lies between $C^{20}H^{10}O^4$ and $C^{20}H^{14}O^4 + H^2O$. The composition of the derivative obtained by heating it with acetic anhydride to 140° – 150° shows that this compound, or at least its chief constituent, has a composition represented by the formula $C^{20}H^{14}O^4$, and that four of its hydrogen-atoms can be replaced by acetyl. This tetracetyl-compound, $C^{20}H^{12}O^4(C^2H^3O)^4$, melts at 148° – 150° , is easily soluble in alcohol and acetic acid, insoluble in water, and easily crystallisable in needles. Liebermann failed to obtain rosaurin from rosaniline, because rosaurin is decomposed by hot water.

Rosaurin and *acetic anhydride* heated in sealed tubes to 150° – 200° do not give rise to an acetyl-rosaurin; but, according to the temperature, various colourless compounds are formed, and among them triacetyl-leucorosaurin, which can be isolated in the pure state and melts at 148° .

Leucorosaurin, $C^{20}H^{18}O^3$, prepared by warming an alkaline solution of rosaurin with zinc-dust till the liquid becomes colourless, separates from the filtrate in brilliant silky colourless crystals. By recrystallisation from dilute alcohol, columnar or acicular crystals are formed, which generally appear brownish. It is easily soluble, in alcohol and ether, especially on heating, but nearly insoluble in water. It gives with alkalis a colourless solution, which, when treated with potassium ferricyanide, assumes the colour of rosaurin, but contains instead a body richer in oxygen. Ferric chloride acts upon it in the same way.

Triacetyl-leucorosaurin, $C^{20}H^{15}O^3(C^2H^3O)^3$, is formed when leucorosaurin is heated with anhydrous acetic acid or acetyl chloride to 130° – 150° . The product of the reaction, when decomposed by water, washed, and crystallised from hot alcohol, deposits triacetyl-leucorosaurin in long needles. This compound is insoluble in water, only slightly soluble in cold alcohol, but moderately soluble in hot alcohol. It melts at 148° – 149° , and solidifies to a glassy mass, which, after a long time, becomes crystalline. When boiled with caustic soda, it shows tolerable stability, but gradually dissolves to a red liquid.

Hydrocyanorosaurin, $C^{21}H^{17}NO^3$, is obtained by acting on the potassium or sodium-derivative of rosaurin with excess of potassium cyanide. Acids precipitate hydrocyanorosaurin from the cold solution in white crystalline flocks, but if the solution is hot, the product cakes together in resinous brownish masses, which gradually become crystalline on cooling. It may be purified by recrystallisation from dilute alcohol. Hydrocyanorosaurin dissolves easily in alcohol, ether, and benzene, but with difficulty in water. Alkalis dissolve it easily to colourless liquids, which become faintly red after long boiling. Its melting point cannot be obtained, since it remains solid at 200° , and decomposes when heated above this point. Concentrated sulphuric acid dissolves it slowly in the cold, readily at a gentle heat, with production of a violet colour, which becomes redder on further heating, and brown when boiled. On heating hydrocyanorosaurin with acetic anhydride to 140° – 150° , a derivative is obtained, which has the composition of *triacetyl-hydrocyanorosaurin*, $C^{21}H^{15}(C^2H^3O)^3NO^3$, is insoluble in water, easily soluble in acetic acid and alcohol, and crystallises in small

colourless prisms which melt at 143° . By strong sulphuric acid it is coloured in the same way as hydrocyanorosaaurin.

Tetrabromorosaaurin, $\text{C}^{20}\text{H}^{12}\text{Br}^4\text{O}^3$, is formed by dropping an excess of bromine into a solution of rosaaurin in warm glacial acetic acid, and separates at once in brownish-green plates having a metallic lustre. The crystals may be freed from rosaaurin by boiling with alcohol, but some compounds containing a smaller amount of bromine remain: these can be removed by recrystallisation from glacial acetic acid.

Tetrabromorosaaurin crystallises from acetic acid, which dissolves it abundantly on heating, in brilliant green plates. When precipitated from its solution by water, or from an alkaline solution by an acid, it forms red microscopic crystals. It is not soluble in water; dissolves with difficulty in alcohol and ether; with a fine violet colour in the fixed alkalis and in ammonia. The absorption spectrum of a moderately deep-coloured ammoniacal solution shows, in addition to a bright band reaching from 30 to 45 (Kirchhoff-Bunsen scale), a second fainter one from 110 to 125. In dilute solutions a faint dark band appears between 50 and 60, while the part of the spectrum corresponding with the above bright streaks is intensely bright. Reducing agents convert this tetrabromo-compound into the corresponding leuco-compound; potassium cyanide forms a hydrocyano-derivative, and alkaline sulphites give rise to colourless solutions, from which the brominated compound is precipitated by mineral acids in red flocks.

Tetrabromoleucorosaaurin, $\text{C}^{20}\text{H}^{14}\text{Br}^4\text{O}^3$, obtained by heating the last-described compound with zinc-dust and caustic soda, is easily soluble in alcohol, and crystallises in plates from weak spirit.

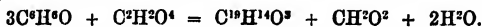
Hydrocyanotetrabromorosaaurin, prepared like hydrocyanorosaaurin, crystallises in colourless plates, insoluble in water, but easily soluble in alcohol and ether. Heated with sulphuric acid, it dissolves with blue colour (Graebe & Caro).

Aurin, $\text{C}^{19}\text{H}^{14}\text{O}^3 = (\text{C}^6\text{H}^4\text{OH})^2\text{C} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{C}^6\text{H}^4 \end{array}$. * *Pararosanolic acid*.—This lower homo-

logue of rosaaurin is formed: 1. By the action of nitrous acid on pararosaniline (p. 1760):



2. Together with formic acid, by heating phenol with oxalic acid in presence of sulphuric acid:



Pure aurin may also be prepared from the commercial product known by the same name (vii. 117), by passing ammonia-gas into a saturated alcoholic solution of the latter, whereupon steel-blue crystals separate out, consisting of ammonia-aurin, $\text{C}^{19}\text{H}^{14}\text{O}^3 \cdot 2\text{NH}^3$; and these, when decomposed by dilute hydrochloric or acetic acid, yield aurin, which, after being well washed and repeatedly crystallised from alcohol, gives by analysis, as a mean result, 78.55 per cent. carbon and 4.96 hydrogen, the formula $\text{C}^{19}\text{H}^{14}\text{O}^3$ requiring 78.62 C, 4.83 H, and 16.55 O.

A further confirmation of this formula of aurin is afforded by its conversion into leucaaurin, which is effected by treating it with acetic acid and zinc-dust. The leucaaurin thus prepared crystallised from dilute alcohol in large flat glistening needles, and when dried over sulphuric acid at 100° , gave by analysis 77.98 and 78.03 per cent. C, 5.68 and 5.7 H, agreeing with the formula $\text{C}^{19}\text{H}^{16}\text{O}^3$, which requires 78.08 C, 5.48 H, and 16.44 O.

Tetrabromaurin, $\text{C}^{19}\text{H}^{10}\text{Br}^4\text{O}^3$, is formed on adding a hot solution of aurin in acetic acid to a mixture of acetic acid and excess of bromine, and separates in small brownish crystals having a bronze lustre. Like tetrabromorosaaurin (*supra*), it dissolves in alkalis with violet colour, and in acid solution dyes silk and wool deep violet.

Compound of Aurin with Acetic Anhydride, $\text{C}^{19}\text{H}^{14}\text{O}^3, \text{C}^4\text{H}^6\text{O}^2$.—This compound is best prepared by gently boiling aurin with acetic anhydride, mixing the resulting yellowish solution with alcohol to decompose the excess of the latter, adding hot water till a precipitate begins to form, and leaving the liquid to cool. The compound then separates out in small white plates melting at 168° . It may also be obtained, though less readily, by heating aurin with acetyl chloride and a little acetic acid till all the excess of acetyl chloride is expelled, and then adding water. It may be boiled with alcohol or acetic acid without alteration, but on adding a small quantity of hydrochloric acid, the solution turns yellow, and on cooling deposits stellate groups of brown needles consisting of a compound not yet analysed.

* Formerly represented by the formula $\text{C}^{19}\text{H}^{14}\text{O}^3$, and supposed to be identical with rosanolic acid (see vi. 299; vii. 117, and this volume, p. 136).

Compound with Hydrochloric acid.—When a hot solution of aurin in acetic acid is saturated with gaseous hydrogen chloride, the liquid assumes a light yellowish-red colour, and soon deposits glistening needles, which smell strongly of acetic acid even when dry, and on exposure to the air acquire a steel-blue lustre, and gradually crumble to a brown-red crystalline powder. This compound, crystallised from acetic acid and dried at the ordinary temperature, has the composition $C^{10}H^{14}O^3, HCl + 2C^2H^4O^2$, the acetic acid playing the part of crystallisation-water. On heating the crystals at 110° in a current of dry air, the whole of the acetic acid is given off, leaving the compound $C^{10}H^{14}O^3, HCl$, which is of a dull red colour, and may be heated to 190° in a current of dry air, without alteration, but begins to give off hydrogen chloride at 200° . When hydrochloric acid gas is passed into an alcoholic solution of aurin, similar but smaller needles are obtained, containing alcohol of crystallisation, and represented by the formula $C^{10}H^{14}O^3, HCl + 3C^2H^4O$. The alcohol is wholly given off at 100° , leaving a dull red residue identical with that above mentioned.

With Sulphuric acid.—The compound $C^{10}H^{14}O^3, SO^2H^2$, is formed on adding a little sulphuric acid to a hot saturated solution of aurin in glacial acetic acid, and separates in prismatic crystals, or in flat, strongly glistening red needles containing acetic acid. An alcoholic solution treated in like manner yields small red needles of the compound $(C^{10}H^{14}O^3)^2, SO^2H^2$ containing alcohol. Both when heated in a current of dry air give off their acetic acid and alcohol respectively, and leave a dull red powder, which is resolved by water into aurin and sulphuric acid. A crystallised *nitrate* has also been obtained.

With Sulphurous acid.—When sulphur dioxide is passed into a hot alcoholic solution of aurin, bright red crystals are obtained of a compound to which Dale & Schorlemmer formerly assigned the formula $(C^{20}H^{14}O^3)^2, SO^2 + 5\frac{1}{2}H^2O$ (p. 119). Subsequent experiments, however, have shown that its true composition when air-dried is $(C^{10}H^{14}O^3)^2, SO^2H^2 + 4H^2O$. When heated in a current of dry air it gives off water and sulphur dioxide. The compounds of aurin with the alkaline bisulphites, $C^{10}H^{14}O^3, SO^2KH$, &c. have been already described (vii. 119).

The compounds of aurin with acids have a red colour like that of aurin itself, whereas those with the acid sulphites and with acetic anhydride are colourless like leucaurin. This seems to show that the members of the two groups differ in constitution.

Corallin. This name is applied to the red product obtained by the action of oxalic and sulphuric acids on commercial phenol (vii. 391). According to Zulkowsky (*Liebig's Annalen*, xciv. 109), it is a mixture of crystalline substances (20 p. c.), viz. *rosolic acid with metallic lustre*, $C^{20}H^{16}O^3$ [rosaurin], a *garnet-coloured rosolic acid*, $C^{10}H^{14}O^3$ [aurin], and amorphous substances (80 p. c.), viz. *pseudorosolic acid* (resinous and *corallin-phthalein*). To separate these substances, the corallin is pulverised, suspended in water, and dissolved by heating the liquid after addition of caustic soda. On passing sulphur dioxide in excess into the solution, it becomes decolorised and deposits the amorphous constituents of the corallin, while the crystalline substances remain dissolved. The solution may be freed from the last traces of resinous matter by adding water and leaving it at rest for several days, and on heating the filtrate with hydrochloric acid to 70° – 80° the rosolic acids [aurin and rosaurin] are set free, and may be separated by washing, drying, and fractional crystallisation from alcohol of 60 per cent., and purified by recrystallisation. The rosaurin crystallises out first, together with a violet needle-shaped compound, then aurin, and lastly leucrosaurin. The violet substance, probably $C^{10}H^{14}O^3 + H^2O$, dissolves in alcohol with brownish-yellow colour, in ammonia and fixed alkalis with crimson colour, and melts at 150° to a brittle mass having a green colour and metallic lustre.

The amorphous bodies consist of colourless pseudorosolic acid and corallin-phthalein. *Pseudorosolic acid*, $C^{20}H^{16}O^4$, to which corallin owes its resinous consistency, is, when recently prepared, a compact more or less reddish mass, which melts very easily, acquiring at the same time a deeper red colour. It dissolves in alkalis with violet-red colour, and by treating the resulting solutions with zinc-dust or sodium-amalgam, and then adding hydrochloric acid, a purer product may be obtained.

Corallin-phthalein, $C^{20}H^{14}O^4$, isomeric with phenol-phthalein, is formed by treating an alkaline solution of pseudorosolic acid with permanganate or ferricyanide of potassium. It is an amorphous, strongly staining powder resembling colcothar, dissolving in alcohol with deep brown-yellow, in alkalis with violet-red colour. In dilute alcoholic solution it has a distinct chatmois-coloured fluorescence. It does not melt at 140° . It is a dye-stuff, imparting to mordanted wool and silk a golden-yellow colour, like that produced by annatto. Its solution in glacial acetic acid yields with bromine a light brick-red tetrabromocorallin-phthalein, $C^{20}H^{10}Br^4O^4$; with nitric acid, a tetranitro-derivative, $C^{20}H^{10}(NO^2)^4O^4$, which dyes wool like picric acid. By heating

with ammonia, it is converted into a red, with aniline into a blue compound. Its hydro-product, boiled with acetic anhydride, is converted into a white amorphous diacetyl-compound, $C^{20}H^{12}O^3(C^2H^4O)^2$, which melts with partial decomposition at 190° .

ROSCOEITE. See VANADATES.

ROSE. The ash of the several parts of a species of garden-rose (*Rosa remontanii*) has been analysed by R. Andreasch (*J. pr. Chem.* [2], xviii. 204), with the following results:

	Roots	Stalks	Leaves	Flowers
K ² O	13.45	14.25	33.13	47.41
Na ² O	4.01	0.15	0.69	1.95
CaO	40.88	51.50	31.29	13.25
MgO	7.15	7.62	9.23	5.34
Fe ² O ³	2.86	4.23	2.39	0.97
Mn ² O ⁴	—	—	traces	traces
Al ² O ³	traces	—	—	—
P ² O ⁵	29.14	10.62	11.68	25.46
SO ³	1.95	2.22	4.31	3.17
SiO ²	0.21	4.85	5.71	1.52
NaCl	0.35	4.56	1.47	0.93
KCl	—	—	—	—
	100.00	100.00	100.00	100.00
Percentage of ash	2.04	2.31	9.43	6.27

ROSE-OIL. This oil is prepared in India and Cashmere by distilling roses with water in earthenware or metal retorts by a current of steam conveyed by a bamboo pipe, mixing the condensed rose-water with a fresh portion of roses, and distilling a second time. As the distillate cools, a thin layer of rose-oil collects on the surface. The oil, when recently taken off, is greenish-yellow, and in the liquid state, after clarification, light yellow with a bright lustre. At 25° or 28° it solidifies to an inodorous camphor or stearoptene (H. von Schlagintweit-Salkülinski, *N. Rep. Pharm.* xxiv. 129).

According to R. Bauer also (*Dingl. pol. J.* cciv. 253), the characteristic odour of rose-oil belongs to the liquid portion, or elaeoptene, whilst the stearoptene is destitute of odour. It is therefore an error to assign the highest value to those samples of the oil which solidify most readily. Rose-oil artificially freed from stearoptene, exhibiting no sign of crystallisation at -15° , and soluble in alcohol of 75 per cent., may be converted into stearoptene by treatment with zinc and alcohol containing a small quantity of strong sulphuric acid. The stearoptene thus obtained melts, like that of natural origin, at 33° .

ROSEMARY-OIL AND CAMPHOR (Bruylants, *J. Pharm.* [4], xxix. 508).

The quantity of essential oil yielded by *Rosmarinus officinalis* depends on the latitude in which the plant is grown, that from the neighbourhood of Paris yielding only 1.4 to 1.6 grams per kilo., whilst that grown in the south of France yields 3 grams per kilo. When freshly prepared, it is a colourless liquid, but darkens in colour and becomes thick on keeping; it is miscible in all proportions with alcohol of 85 per cent. It smells strongly of rosemary, tastes hot and camphorous; has a density of 0.885 at 12° ; turns the plane of polarisation to the left. It begins to boil at 150° , the temperature gradually rising to 200° , where it remains stationary for a short time, and finally rises to 260° . By fractional distillation, the oil may be separated into three portions, boiling from 150° to 180° , from 180° to 210° , and from 210° to 260° .

Fraction boiling between 150° and 180° .—By repeated distillation and rectification over sodium, a liquid is obtained boiling at 157° – 160° , which is lavogyrate. Its vapour-density corresponds with the formula for terpene, $C^{10}H^{16}$. This terpene combines with iodine, and on distilling the product, it decomposes into hydriodic acid and cymene, $C^{10}H^{14}$; by the action of nitric acid, it yields α -toluic acid.

Fraction boiling between 180° and 210° .—By careful distillation, a liquid boiling at 200° – 205° is obtained, which on cooling deposits crystals melting at 176° and boiling at 204° . They exhibit all the properties of laurel camphor. The mother-liquor boils at a lower temperature, and on distillation yields a second crop of crystals and some terebene. Repeated distillation results in the complete separation of these two bodies.

Fraction boiling between 210° and 260° .—On cooling this fraction in a freezing mixture, a large quantity of borneol separates out, which when treated with phosphoric

anhydride, yields a hydrocarbon boiling at 160° , and having the vapour-density 5.23. This, when treated with iodine, yields cymene and hydriodic acid. Amongst the products of the action of nitric acid are borneol, and a crystalline body which melts at the same temperature as camphor. The borneol, distilled with acetic anhydride, yields a product boiling at 230° , which is decomposed by potash, with formation of a hydrocarbon, $C^{10}H^{16}$, and potassium acetate.

Essence of rosemary therefore contains:

A hydrocarbon (lævogyrate), $C^{10}H^{16}$	80 per cent.
A borneol camphor, $C^{10}H^{18}O$	4 to 5 „
A camphor, $C^{10}H^{18}O$	6 to 8 „

When acted on by concentrated sulphuric acid, essence of rosemary yields a mixture of cymene (b. p. 175°), and terpene (b. p. 16°), and on oxidation with chromic mixture, a small quantity of camphor, some formic and acetic acids, and terephthalic acid.

RUBEOSIN. See PHTHALEÏN-DYES (p. 1614).

RUBIDIUM and CÆSIUM. On the preparation of these metals from lepidolite, see H. Peterson (*Dingl. pol. J.* cccxiii. 111; *Chem. Soc. J.* xxxii. 706). According to Cossa (*Gazz. chim. ital.* 1878, 235), the alum of the island of Vulcano is—with exception of the very rare mineral, pollux—the richest known source of cæsium and rubidium. On the separation of these metals from it, see p. 1331.

Solubility of Rubidium and Cæsium salts.—On comparing the solubility of these salts with the corresponding salts of the other alkali-metals, it is found that nearly all the simple salts of cæsium and rubidium are considerably more soluble than those of the other alkali-metals, and that, on the contrary, the double salts of cæsium and rubidium, as well as those which contain complex acid radicles, are much less soluble than the corresponding salts of the other alkali-metals (Godeffroy, *Ber.* ix. 1363).

The following salts of these metals have been examined by Godeffroy (*Liebigs Annalen*, clxxxii. 176; *Ber.* ix. 1363; *Arch. Pharm.* [3], xii. 47), in addition to those already described (p. 368).

Chlorides. *Cæsioplatinous Chloride*, $2CsCl, PtCl_2$, is formed by heating cæsioplatinic chloride to fusion with oxalic acid, or in a stream of hydrogen, and separates on evaporating the red solution filtered from metallic platinum, in long monoclinic prisms, permanent in the air, dark-red by transmitted, green by reflected light, and exhibiting a fine play of colours. They melt without alteration, but are decomposed at a red heat into cæsium chloride, metallic platinum, and free chlorine. They are moderately soluble in water, insoluble in alcohol. 100 pts. of water dissolve the following quantities of the salt:

at	20°	40°	60°	80°	100°
	3.4	6.73	8.68	10.92	12.10 parts

The yellowish-red solution is not altered by boiling, but is partially decomposed on addition of alcohol, more completely when boiled with glycerol, whereby indeed the whole of the platinum may be precipitated from the solution. The crystals are rhombohedrons with rounded edges. *Cæsiopalladious chloride*, $2Cs, PdCl_2$, crystallises from aqueous solution in tufts of dark red-brown highly lustrous needles. The solution is decomposed by boiling, the whole of the palladium being precipitated as a black powder.

Cæsiauric chloride, $CsCl, AuCl_3$, forms small reddish-yellow needle-shaped crystals, somewhat sparingly soluble in water, alcohol, and ether.

Cæsiomanganous chloride, $CsCl, MnCl_2$, is obtained as a crystalline anhydrous precipitate on mixing the solutions of the two salts in hydrochloric acid, and the mother-liquor, when left to evaporate, yields small reddish monoclinic prisms of the hydrated salt $2(CsCl, MnCl_2) + 5H_2O$.

Rubidium chloride, $RbCl$, crystallises in forms of the regular system, the cube predominating.

Rubidium-antimony chloride, $6RbCl, SbCl_3$, forms hexagonal plates exhibiting the combination 0P.P, with ∞P subordinate. The P-faces are deeply striated in the horizontal direction. The angles of the lateral edges are equal to $129^{\circ} 30'$, whence $a : c = 1 : 1.8336$. *Rubidioferric chloride*, $6RbCl, Fe_2Cl_6$, is obtained by evaporating a solution of the two chlorides with a little hydrochloric acid, in small yellowish-red orthorhombic crystals, permanent in the air, very soluble in water, separated by concentrated hydrochloric acid as a yellowish-red precipitate.

Rubidio-manganous chloride, $2RbCl, MnCl_2 + 3H_2O$, separates, on slow evaporation of the mixed aqueous solutions of the component chlorides, in large pale red crystals easily soluble in water, insoluble in alcohol. From its concentrated solution it is

precipitated by strong hydrochloric acid as an anhydrous crystalline powder. *Rubidio-cadmie chloride*, $2\text{RbCl}, \text{CdCl}_2$, is obtained as a crystalline deposit on mixing the solutions of the two chlorides in hydrochloric acid. If, however, the cadmium chloride is in excess, another double salt, $2(\text{RbCl}, \text{CdCl}_2) + \text{H}_2\text{O}$, separates in long hard needles having a silky lustre; and on evaporating the mother-liquor to dryness, and dissolving the residue in water, the salt $4(\text{RbCl}, \text{CdCl}_2) + \text{H}_2\text{O}$ is obtained in large well-defined prisms. *Rubidio-mercuric chloride*, $2\text{RbCl}, \text{HgCl}_2$, is obtained, on mixing the neutral solutions of the two salts and evaporating, in small anhydrous needle-shaped crystals; and on dissolving these in water, and leaving the solution to evaporate, the hydrated salt, $2\text{RbCl}, \text{HgCl}_2 + 2\text{H}_2\text{O}$, separates in large colourless prisms. The salt $\text{RbCl}, 2\text{HgCl}_2$ is obtained on evaporating the aqueous solution of equal weights of the component chlorides, as a thick crystalline pulp of silky needles. When heated to 50° , it gives off half of the mercuric chloride, and is converted into $\text{RbCl}, \text{HgCl}_2$.

Rubidio-auric chloride, $\text{RbCl}, \text{AuCl}_3$, is obtained on mixing the moderately dilute solutions of the component chlorides, as a golden-yellow precipitate, the aqueous solution of which yields the salt on evaporation in long golden-yellow prismatic crystals resembling those of saltpetre. When heated it first changes into reddish-brown rubidio-aurous chloride, and at a red heat is easily and completely resolved into rubidium chloride and metallic gold (Godeffroy, *Arch. Pharm.* [3], xii. 47).

Silicotungstates. On mixing an aqueous solution of caesium chloride with silicotungstic acid (v. 916), a white crystalline precipitate is formed, which, when washed and dried, has the composition $\text{SiW}^{12}\text{O}^{42}\text{Cs}^3$, or $4\text{Cs}_2\text{O}, \text{SiO}_2, 12\text{WO}_3$. 100 pts. of water dissolve only 0.005 pt. of this salt at 20° , and 0.52 at 100° , or 1 pt. of the salt dissolves in 20,000 pts. of water at 20° , and in 192–200 pts. at 100° . The salt is quite insoluble in alcohol and in water containing hydrochloric acid, but dissolves to a not inconsiderable amount in dilute ammonia.

The corresponding *rubidium salt*, obtained in like manner, is a white precipitate; 100 pts. water dissolve 0.69 pt. of it at 20° , and 5.06 pts. at 100° , or 1 pt. of the salt dissolves in 145–150 pts. of water at 20° , and in 19–20 pts. at 100° . It is insoluble in alcohol, sparingly soluble in water containing hydrochloric acid, but extremely soluble in ammoniacal water (Godeffroy, *Ber.* ix. 1363).

Monorubidium Dioxalate, $\text{RbHC}_2\text{O}_4, \text{C}^2\text{H}^2\text{O}_4$. See OXALATES (p. 1454).

RUBIJERVINE, $\text{C}^{26}\text{H}^{42}\text{NO}^2$. See VERATRUM ALKALOIDS.

RUBY and SAPPHIRE. *Artificial Formation.*—When a mixture of equal parts of alumina and minium is heated to redness in a crucible, a vitreous substance is produced consisting of lead silicate (the silica being derived from the crucible), together with white corundum crystallised in hexagonal prisms. An addition of 2 or 3 per cent. potassium dichromate converts this white corundum into ruby, and a little cobalt oxide with a trace of the dichromate yields sapphires. The crystals scratch quartz and topaz, and have a sp. gr. of 4.0–4.1. The artificial rubies, like the natural gems, are transiently decolorised by ignition. Another mode of operating is to use two crucibles, the lower containing a mixture of equal parts of alumina and barium fluoride, the upper serving as a cover. At the termination of the experiment, rose-red rubies are found in the lower crucible, while the upper contains colourless, long, or sometimes shorter, monoclinic prisms, consisting of 34.32 per cent. SiO_2 , 35.04 BaO, and 30.37 Al_2O_3 . The reaction consists in the formation, in the first instance, of baryta and aluminium fluoride, which latter is resolved into alumina and hydrogen fluoride, but must at the same time serve as a means of transport to the baryta, which, together with a portion of the alumina and silica from the crucible, forms the double silicate (Frémy a. Foil, *Compt. rend.* lxxxv. 1029).

RUFIGALLOL, or *Hexhydroxy-anthraquinone*,



Rufigallic acid.—This view of the constitution of rufigallol, first suggested by Jaffé (*Ber.* iii. 964), is supported by the fact that it is reduced by sodium-amalgam to alizarin (dihydroxyanthraquinone) (Jaffé, *loc. cit.*; O. Widmann, *Ber.* viii. 109), and by heating with zinc-dust to anthracene, $\text{C}^{14}\text{H}^{10}$ (Jaffé, *loc. cit.*; Klobukowski a. Nölting, *ibid.* 819, 831). According to Schiff's view, who regards rufigallol as digallic anhydride (vii. 1062), it should be convertible into gallic acid; this conversion, however, was found by Klobukowski a. Nölting not to be produced either by hydrochloric acid at 250° , or by potash-ley at 200° . Moreover, when heated to 250° with acetic anhydride, it yields a hexacetyl-derivative, $\text{C}^{14}\text{H}^2(\text{C}^2\text{H}^3\text{O})^6\text{O}^8$. Rufigallol, boiled with excess of monochloroacetyl chloride, exchanges only 1 at. hydrogen for chloroacetyl, forming the compound $\text{C}^{14}\text{H}^7(\text{C}^2\text{H}^2\text{ClO})^6\text{O}^8$, which is insoluble in water, alcohol, benzene, and carbon sulphide, and slightly soluble in glacial acetic acid, from which it crystal-

lises in yellow-brown microscopic needles; in strong potash-ley it dissolves with indigo-blue colour, in strong sulphuric acid with blue colour (Klobukowski, *Ber.* x. 880).

Rufgallol is not acted upon by tin and hydrochloric acid, but when heated for an hour or two with excess of hydriodic acid (sp. gr. 1.96) and white phosphorus to the boiling point of the hydriodic acid, it is converted into the compound $C^{14}H^{10}O^7$, which forms a yellow powder, consisting of microscopic needles insoluble in the ordinary solvents, but dissolving in strong sulphuric acid to a greenish-blue liquid (changing when further heated to blue and then to violet), from which water throws down greenish-yellow flocks. In contact with water and sodium-amalgam, this compound dissolves, forming a red liquid. When distilled with zinc, it yields anthracene. When boiled with *acetic anhydride*, it yields an acetyl-derivative, $C^{14}H^4(C^2H^3O)^4O^7$ [?], which dissolves in glacial acetic acid with splendid blue fluorescence, crystallises from the solution in greenish-yellow needles, and dissolves in sulphuric acid with green colour changing to blue (Klobukowski, *Ber.* ix. 1256).

Methyl- and Ethyl-derivatives. Rufgallol, heated for three or four hours at 120° – 130° with excess of methyl iodide, potash, water, and a small quantity of methyl alcohol, is converted into a red mass, which, when crystallised from acetic ether, yields laminae having a golden lustre, or lancet-shaped needles consisting of tetramethylrufgallol, $C^{14}H^{10}O^8 = C^{14}H^4(CH^3)^4O^8$. This compound is insoluble in ether, sparingly soluble in boiling alcohol, easily in ethyl acetate and glacial acetic acid. When boiled with a strong alkaline ley it dissolves slowly, forming a red liquid; strong sulphuric acid, on the other hand, dissolves it readily on boiling, forming a crimson solution from which water throws down yellow flocks. It melts at about 220° . Tetraethyl-rufgallol, $C^{14}H^4(C^2H^5)^4O^8$, prepared in like manner with ethyl iodide, is somewhat sparingly soluble in boiling alcohol, and crystallises therefrom in ruby-red needles. It dissolves sparingly in ether, easily in chloroform, benzene, ethyl acetate, and hot glacial acetic acid; reacts with alkalis, and strong sulphuric acid like the tetramethyl-compound; melts at a temperature a little above 180° . By further digestion with ethyl iodide and potash, it is converted into hexethyl-rufgallol, $C^{14}H^2(C^2H^5)^6O^8$, which crystallises in orange-yellow needles easily soluble in ether, carbon sulphide, benzene, hot glacial acetic acid, and hot dilute alcohol, and melts at about 140° ; it is insoluble in alcohol, but dissolves with crimson colour in sulphuric acid (Klobukowski, *Ber.* xi. 880).

RUFHYDROELLAGIC ACID, $C^{14}H^4O^8$. See ELLAGIC ACID (p. 730).

RUTHENIUM. According to Deville a. Debray (*Compt. rend.* lxxx. 457), ruthenium tetroxide decomposes at 108° with violent explosion, producing a thick black smoke like that which is given off in the combustion of turpentine-oil, and a strong odour of ozone. On the other hand, this oxide is formed when ruthenium is heated in the oxy-hydrogen blowpipe, ozone being produced in this case. Ruthenium dioxide, heated in a stream of oxygen at a temperature somewhat above that of melting copper, is converted into very finely developed crystals, ruthenic anhydride being perhaps temporarily formed.

RUTILE. See TITANIUM.

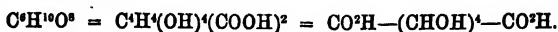
RUTILYDENE, syn. with *Nonylacetylene*, $C^{11}H^{20} = C^8H^{10}C \equiv CH$ (p. 1421).

RYE. *Secale cereale*.—A. Muntz (*Compt. rend.* lxxxvii. 679) has found in unripe rye-grain a peculiar substance called *synanthrose* (as it is also found in several synanthaceous or composite plants), convertible by boiling with dilute sulphuric acid into levulose (see SUGARS). It disappears as the grain ripens, being converted into starch.

To detect ergot in rye-flour, R. Böttger (*Zeitschr. anal. Chem.* 1874, 80) treats a sample of the flour in a test-tube with an equal volume of ether, adds a few crystals of oxalic acid, and heats the whole for a few minutes to boiling. If ergot is present, the solution exhibits a more or less reddish colour.

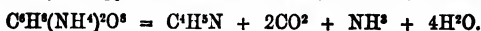
S.

SABADILLA. On the Alkaloids of Sabadilla seeds, see VERATRUM ALKALOIDS.
SACCHARIC ACID,



Action of Phosphorus Pentachloride.—According to Wichelhaus (*Liebigs Annalen*, cxxxv. 252), the action of PCl_5 on cadmium saccharate does not give rise to any organic chloride. C. J. Bell, however (*Ber.* xii. 1271), by substituting the potassium salt for the cadmium salt, has obtained chloromuconic acid, $\text{C}^6\text{H}^4\text{Cl}^2\text{O}^4$, crystallising from alcohol in long silky needles, sparingly soluble in ether and in water, melting at 250° , and agreeing in other respects, and in the properties of its ethylic ether, with the chloromuconic acid obtained from mucic acid (vii. 827).

Ammonium saccharate, slowly distilled at the heat of a paraffin-bath, breaks up almost quantitatively into pyrroline, carbon dioxide, ammonia, and water:



Ethylamine saccharate is also decomposed in a similar manner, yielding ethyl-pyrroline in theoretical amount. No trace of any carboxylated derivative of pyrroline appears to be formed in either case. For these reactions, saccharic acid is distinguished from its isomeride, mucic acid, the amine salts of which, when heated, yield alkyl-derivatives of pyrroline, together with the alkylamides of the mono- and di-carboxylated derivatives of these pyrrolines (see PYRROLINES, p. 1728) (C. A. Bell & E. Lapper, *Ber.* x. 1961).

SACCHARITE. Glocker in 1845 (*J. pr. Chem.* xxxiv. 494) described a mineral which he named saccharite, from its granular, sugar-like appearance. It was originally found on the Gläserdorfer Berg, near Frankenstein in Saxony, in a chrysoprase mine. According to Glocker, saccharite encloses pinchbeck-brown mica-scales, small plates of talc, green fibrous hornblende, long isolated tourmaline crystals, and finely divided disseminated iron pyrites, the surface of the specimens being generally coated with a crust of green pimeleite. According to an analysis by C. Schmidt (v. 144), saccharite is a felspar most nearly approaching andesine in composition. A. v. Lasaulx (*Jahrb. f. Min.* 1878, 623) obtained some specimens of a mineral (which appeared to be identical with saccharite in its physical properties) from the five serpentine mounds of the Gumburg, near Frankenstein, and examined them microscopically, together with the original specimen described by Glocker. Glocker's saccharite consists mostly of fine-grained plagioclase, exhibiting a very distinct twin-striation, and optical properties closely resembling those of oligoclase or andesine; next in amount comes orthoclase, then hornblende and tourmaline crystals, whilst in one specimen (in addition to the minerals already mentioned) minute fibres of talc were observed. Some specimens of saccharite from the Wachberg, near Baumgarten, contained a large quantity of round quartz-grains, together with plagioclase, and a few isolated epidote grains. The Gumburg saccharite differs considerably in its microscopical character from that of the other localities, although its outward appearance is almost identical with that of Glocker's saccharite, some specimens being white, with a green coating of pimeleite, whilst others have a yellowish, reddish, or deep red colour. Quartz was found to be the predominating constituent of Gumburg saccharite. The yellowish-red specimens were found to be a mixture of predominating quartz, with a small quantity of plagioclase, and a small quantity of colourless, granular garnet, diopside, and epidote. The garnet grains are generally arranged in rows, one behind the other, but they sometimes occur in bands and lenticular forms, in conjunction with granular quartz-aggregates. They seldom enclose other minerals, quartz being the only exception. The brown-red saccharite owes its colour to ferric oxide, which is evenly distributed throughout the mass. The felspar grains did not exhibit any signs of decomposition in any of the specimens, a fact which is at variance with the opinion that 'saccharite is a felspar very much altered, and undergoing decomposition' (*Blum. Min.* 2. Aufl. 310). From microscopical examination of the various varieties of saccharite, v. Lasaulx is of opinion that it cannot any longer be considered as a distinct plagioclase species, but only as a rock-like variable mixture of plagioclase with other minerals, because the plagioclase almost disappears in some cases; and he concludes from its peculiar occurrence in the serpentine rocks, that it is a product of the decomposition of hornblende rocks.

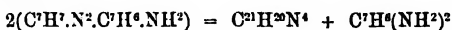
SACCHAROSE. See SUGAR.

SAFRANINE, $C^{21}H^{20}N^4$. This name has been given to a red colouring matter (also called 'aniline-pink'), obtained by Perkin as a product of the oxidation of mauveine; also to a product which Hofmann a. Greyer obtained by treating orthotoluidine, or crude aniline containing it, first with nitrous acid, and then with arsenic acid, or better with chromic acid (vii. 1063). Subsequent researches, however, by Dale a. Schorlemmer (*Chem. Soc. J.* xxxv. 683), and by Perkin (*ibid.* 728), have shown that the products formed in these two processes are not identical but homologous, the body obtained from orthotoluidine having the composition $C^{21}H^{20}N^4$, and being formed as already pointed out (vii. 1063), according to the equations $3C^7H^5N + NO^2H = 2H^2O + C^{21}H^{20}N^4$, and $C^{21}H^{20}N^4 + O^2 = 2H^2O + C^{21}H^{20}N^4$, whereas the colouring matter obtained by oxidation of mauveine has the composition $C^{20}H^{18}O^4$, and is probably formed according to the equation:



The name safranine is now therefore restricted to the higher homologue (C^{21}), while the lower (C^{20}) is called *parasafranine*.

Safranine is also produced in considerable quantity, together with paratolylene-diamine, by heating amidazortholuene with orthotoluidine hydrochloride in alcoholic solution at $150^\circ - 160^\circ$:



(O. N. Witt, *Ber.* x. 873).

Safranine is now used extensively in the dyeing of silk, and according to R. Böttger (*N. Rep. Pharm.* xxiii. 181) is easily obtained chemically pure by treating the commercial product with alcohol. It then forms a powder having a greenish surface-shimmer and metallic lustre, and possessing extraordinary tinctorial power. A peculiar and beautiful play of colours may be produced by sprinkling a few particles of the powder in a porcelain capsule with a drop or two of strong sulphuric acid, stirring it at the same time with a glass rod, whereupon a most splendid blue colour is produced which, on addition of a drop or two of water, changes to a brilliant emerald-green, and by alternately dropping in sulphuric acid and water, almost all the colours of the spectrum may be produced in great beauty.

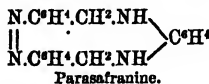
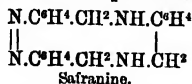
The following process for distinguishing safranine from magenta-fuchsine of similar hue, is recommended in Reinmann's 'Färbezeitung' and *Dingl. pol. J.* cxxii. 531. If the dye-stuff is in the solid state, a few grains of it may be placed on a watch-glass and sprinkled with 6 drops of strong sulphuric acid, which will dissolve fuchsine with brown-red colour, whereas with safranine the solution will at first exhibit a green colour, changing to a fine blue. A solution of safranine in alcohol exhibits by transmitted light a clear roseate hue, in reflected light a muddy ponceau to scarlet colour; a solution of fuchsine does not exhibit this dichroism. Dyed stuffs may be boiled with alcohol, which takes up the colouring matter, or they may be treated as follows: Stuffs dyed with fuchsine become lighter in colour when warmed with dilute soap-solution, and are completely decolorised by warming with solution of sodium carbonate, whereas those dyed with safranine are not altered by either mode of treatment. On drenching the dyed stuff with water containing hydrochloric acid, and immersing a plate of zinc in the liquid, fuchsine is decolorised as soon as the evolution of hydrogen begins, whereas safranine remains unaltered for a few minutes and ultimately turns yellow.

Parasafranine, $C^{20}H^{18}N^4$, is obtained, as already observed, by oxidation of mauveine. Perkin prepares the hydrochloride, $C^{20}H^{18}N^4.HCl$, by dissolving mauve dye in water acidulated with hydrochloric acid, keeping the solution at the boiling heat, adding freshly precipitated lead dioxide by small portions till the oxidation has proceeded far enough, then adding sodium hydrate in slight excess, filtering, boiling the red filtrate for a short time with a little powdered zinc and calcium carbonate, again filtering, slightly acidifying with hydrochloric acid, and adding a little sodium chloride to facilitate the precipitation of the colouring matter. The hydrochloride is thus obtained as a red-brown precipitate, dissolving in water and alcohol with a splendid red colour, and giving by analysis 67.96 per cent. carbon, 5.56 hydrogen, and 10.21 chlorine, the formula requiring 68.44 C, 5.42 H, and 10.41 Cl. Similar results have been obtained by Dale a. Schorlemmer. The other salts of parasafranine are prepared by mixing the solution of the hydrochloride in boiling water with a slight excess of caustic alkali, then acidifying with the required acid, and, if necessary, saturating the solution with a soluble salt of the same acid. The *oxalate* thus prepared may be obtained in needles of a dark green metallic aspect by adding oxalic acid and leaving the solution at rest. The *nitrate*, $C^{20}H^{18}N^4.HNO^3$, crystallises beautifully from alcohol in long needles having a dark green metallic reflex, and appearing

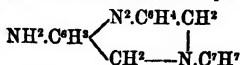
of a dark garnet-red colour by transmitted light. It dissolves somewhat sparingly in cold water, with moderate facility in boiling water and in cold alcohol, freely in boiling alcohol.

Safranine salts differ from those of parasafranine in the colour which they impart to silk, yielding shades which are somewhat more scarlet (Perkin).

The following formulæ are suggested by Perkin as probably representing the constitution of safranine and parasafranine:



O. N. Witt, on the other hand, represents safranine by the constitutional formula:



SAFROL. See SASSAFRAS-OIL.

SAFROSIN. A colouring matter belonging to the resorcinol-group, and prepared by dissolving 9 kilos. of tetrabromofluorescein in alkaline water, adding 8 kilos. sodium nitrate, heating the mixture to boiling, and then adding 15 kilos. of sulphuric acid 66° B. The precipitate is filtered off, washed, dissolved in dilute soda-ley, and evaporated. The salt thus obtained dyes wool with a more bluish-red tinge than tetrabromofluorescein (Bindschedler u. Busch, *Chem. News*, xxxviii. 226).

SAGAPENUM. All varieties of this resin when moistened with alcohol and treated with strong sulphuric acid dissolve with dark brown colour, the solution sometimes becoming carmine-red at the edges; on addition of alcohol, the colour changes to light brown-red, violet, and sometimes blue. Hydrochloric acid added to sagapenum moistened with alcohol produces a yellowish-red or sometimes rose-red coloration passing into violet, blue-violet, or even blue. Sagapenum distilled with steam yields 7.5 per cent. of a sulphuretted oil smelling like garlic. Petroleum ether dissolves sagapenum more abundantly than galbanum or gum ammoniacum, the dissolved portion consisting of volatile oil and resin, and containing sulphur (Hirschsohn, *Jahresb. f. Chem.* 1875, 859).

SAGE-OIL. The volatile oil of *Salvia officinalis* has been examined by Muir u. Sigiura (*Phil. Mag.* [5], iv. 336; *Chem. Soc. J.* xxxiii. 292), and further by Muir (*Chem. News*, xli. 223). The composition of the oil varies with its age. When freshly distilled, it contains comparatively small quantities of salviol, $\text{C}^{10}\text{H}^{18}\text{O}$, camphor, and cedrene, but as it ages, these substances increase in quantity, especially the first two. The oil distilled from English sage contains much cedrene boiling at 260°, together with small quantities of terpene, and traces of oxidised compounds. The terpene of sage-oil is identical with that obtained from French turpentine; an isomeride of terpene, boiling at 171°, appears also to be present.

Salviol, $\text{C}^{10}\text{H}^{18}\text{O}$, has a sp. gr. of 0.934 at 15°, and a refractive index for the line D at 20°, equal to 1.4623; hence specific refractive energy = 0.495. A column 100 mm. long rotates the polarised ray 15.13° to the right; hence specific rotatory power = +16.19. Phosphoric anhydride exerts on salviol a very complex action, yielding polymerides of $\text{C}^{10}\text{H}^{18}$, one boiling at 171°, a hydrocarbon of the benzene series boiling below 130°, and a paraffin boiling between 170° and 180°; no cymene is formed, even if the action be continued for some time. Phosphorus pentachloride acts on salviol at high temperatures, producing a chlorinated derivative which is decomposed by distillation, yielding a terpene boiling at 157°, and probably the paraffin above mentioned. Bromine acts energetically on salviol, with liberation of hydrogen and carbon, and formation of a brominated oil, and, under certain conditions, small quantities of a camphor melting at 174°, and boiling at 205°. This camphor separates also from the portions of sage-oil distilling between 205° and 208°; it is partially soluble in salviol, but separates out on cooling the solution to -15°. It is chemically identical with laurel camphor, but is optically inactive.

The compounds present in sage-oil are stable when pure, but decompose when mixed with small quantities of other bodies; and during the ageing and fractionation of the oil, processes of oxidation, deoxidation, and polymerisation probably occur simultaneously.

SAXI. An alcoholic drink prepared in Japan from rice. For the mode of preparation, see O. Korschelt (*Dingl. pol. J.* cxxx. 76, 172, 229, 330, 421; *Chem. Soc. J.* xxxvi. 413).

SALICYLIC, or ORTHO-HYDROXYBENZOIC ACID, $\text{C}^6\text{H}^4.\text{OH}.\text{CO}^2\text{H}.\text{H}^4$. (See pp. 278, 1461).

SALICYLURIC ACID, $C^6H^5NO^4$. This acid has been found, together with salicylic acid, in the urine of fever patients to whom large doses of salicylic acid had been administered. The two acids are best separated by treatment with a mixture of ether and benzene, in which salicylic acid dissolves more readily than salicyluric acid. From the aqueous solution of an impure mixture of the two, the salicyluric acid crystallises out last on cooling (Beck, *Ber.* viii. 817).

SALIRETIN, C^6H^5O , is produced by the action of sodium-amalgam on para-hydroxybenzoic acid; salicylic acid appears to yield an isomeric compound (A. von den Velden, *J. pr. Chem.* [2], xv. 163). The glucoside of saliretin appears to be formed by the action of acetochlorhydrase on sodium-amalgam (A. Michael, *Compt. rend.* lxxxix. 355).

SALITE. This mineral, from the granular limestone of Albrechtsberg in Lower Austria, where it occurs in groups of crystals 12 cm. long, has been analysed by E. v. Bamberger (*Min. Mitth.* 1877, 273). A. analysis; B. values calculated from the formula $MgCaSi^2O^4$:

	SiO^2	Al^2O^3	FeO	CaO	MgO	Sp. gr.
A.	55.60	0.16	0.56	26.77	18.34 = 101.43	3.167
B.	55.56	—	—	25.92	18.52 = 100	

According to E. Kalkowsky (*Jahrb. f. Min.* 1875, 755), salite is a widely diffused constituent of crystalline slates, also of the chloritic gneiss of Silesia, the dioritic slates of Kupferberg, the mica slate of Waltersdorf near Kupferberg, the hornblende slate of Raspenau in Bohemia, and of the erlan of Schwarzenberg in the Erzgebirge.

SALTS. The specific gravities of a large number of salts have been determined by students working under the direction of F. W. Clafke, and published by him in *Silliman's Journal*, [3], xv. 281. The weighings were made in benzene, but the numbers all refer to water at its maximum density as unity.

BaI^2O^6	5.2179, 5.1853, 5.2855 at 18°.
$AgIO^3$	5.4023 at 16.5°; after recrystallisation from ammonia, 5.6475 at 14.5°.
PbI^2O^6	6.1783 at 19°; 6.1322 at 21°.
NH^4IO^3	3.3085 at 21°; 3.3372 at 12.5°.
CdI^2	5.9857 at 12°; 5.9738 at 13.5°.
BiI^3	5.9225 at 16°; 5.8813 at 17.5°.
K^2NiCy^4, H^2O	1.875 at 11°; 1.871 at 14.5°.
$K^2PtCy^4, 3H^2O$	2.5241 at 13°; 2.4548 at 16°. Crystals slightly moist.
NH^4CyS	1.299 and 1.316 at 13°.
$K^4CrCy^{12}S^{12}, 8H^2O$	1.7051 at 17.5°; 1.7107 at 16°.
$K^2PtCy^4S^4$	2.370 at 19°; 2.342 at 18°.
Sodium nitroprusside	1.6869 at 25°.
$NiN^2O^4, 6H^2O$	2.065 at 14°; 2.037 at 22°.
$ZnN^2O^4, 6H^2O$	2.063 at 13°; 2.067 at 15°.
$CdN^2O^4, 4H^2O$	2.450 at 14°; 2.460 at 20°.
$BiN^2O^4, 5H^2O$	2.823 at 13°.
$KBrO^3$	3.323 at 19°.
$AgBrO^3$	5.1983 at 16°.
$BaBr^2O^6$	4.6395 at 17°.
CaS^2O^3	1.8715 at 13.5°.
$SrS^2O^3, 6H^2O$	2.1566 at 17°.
BaS^2O^3, H^2O	3.4461 at 16°.
$BaP^2H^4O^4, H^2O$	2.8718 at 10°.
$MgP^2H^4O^4, 6H^2O$	1.5886 at 12.5°.
$NaPO^3$	2.4756 at 19.5°.
KPO^3	2.2639 at 14.5°.
Na^2WO^4	4.1743 at 20.5°.
$Na^4WO^4, 2H^2O$	3.2588 at 17.5°.
$BaWO^4$	5.0035 at 13.5°.
$NiWO^4$	6.8846 at 20.5°.
$BaMoO^4$	4.6589 at 17.5°.
$SrMoO^4$	4.1654 at 20.5°.
Na^3PO^4	2.5111 at 12°.
$Na^4P^2O^7, 10H^2O$	1.7726 at 21°.
$MgCrO^4, 7H^2O$	1.7613 at 16°; at 130° 6 mols of water go off; the 7th mol. cannot be driven off without decomposing the salt.

$(\text{NH}_4)_2\text{CrO}_4$	1.9138 at 12°.
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	2.1223 at 16°.
Na_2CrO_4	2.7353 at 12°.
$(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.8278 at 16°.
$\text{K}_2\text{Mg}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$	2.5804 at 19°.
Cr_2Cl_6 (well crystallised)	2.3572 at 17.5°; 2.3766 at 16.5°; 2.349 at 20°.

The molecular volumes of these chromates are almost identical with those of the corresponding selenates.

$\text{Mn}^{2+}\text{P}_2\text{O}_7$	3.5847 at 20°.
$\text{Zn}^{2+}\text{P}_2\text{O}_7$	3.7538 at 23°.
$\text{Ni}^{2+}\text{P}_2\text{O}_7$	3.9403 at 25°.
$\text{Zn}^{2+}\text{As}_2\text{O}_7$	4.7034 at 21°.
$\text{Be}^{2+}\text{O}_4 \cdot 4\text{H}_2\text{O}$	1.6743 at 22°.
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	2.634 at 24°.
$\text{Hg}(\text{C}^1\text{H}^1\text{O}_2)_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$	3.2336 at 21°.
KIO_3	3.802 at 18°.
TeO_3	5.0704 at 14.5°.
$\text{Mg}^{2+}\text{P}_2\text{O}_7$	2.5988 at 22°.
$\text{Co}^{2+}\text{P}_2\text{O}_7$	3.746 at 23°.
$\text{Mn}^{2+}\text{As}_2\text{O}_7$	3.6832 at 23°.
$\text{Mg}^{2+}\text{As}_2\text{O}_7$	3.7305 at 15°.
$\text{CrK}^3\text{C}^6\text{O}^{12} \cdot 3\text{H}_2\text{O}$	3.1039 at 23°.
HgI^2CuI	6.1602 at 15°.
$\text{Hg}(\text{C}^2\text{H}^2\text{O}_2)_2$	3.2544 at 22°.
TeO_7	5.7559 at 12.5°.
BaTeO_4	4.5486 at 10.5° (feebly ignited).

* On the Melting Points of Metallic Salts, see Carnelley (p. 937).

Diffusion of Salts in Solution.—The simultaneous diffusion of salts which do not act chemically on one another—in other words, of such as contain the same base or the same acid—has been investigated by Marignac (*Ann. Chim. Phys.* [5], ii. 546; *Chem. Soc. J.* xxviii. 35; *Jahrsb. f. Chem.* 1874, 37) in an elaborate series of experiments, the main result of which is to confirm Graham's observation that in a mixture of two salts, the diffusibility of the less diffusible is diminished, while that of the more diffusible is in some cases slightly increased, in others diminished, but always in a smaller degree than that of the less diffusible salt. This mutual influence becomes less as the solutions are more dilute, but the limit towards which dilution tends to bring the ratio of the coefficients of simultaneous diffusion does not coincide with the ratio of the coefficients of separate diffusion, except in the following cases: The chlorides of potassium, sodium, and ammonium in presence of the corresponding nitrates; sodium chloride and ammonium chloride; potassium nitrate and ammonium nitrate; the sulphates of potassium and ammonium in presence of magnesium sulphate.

Mixtures of two salts which are capable of forming double salts— K_2SO_4 and MgSO_4 , for example—exhibit no tendency to diffuse in equivalent proportions: hence it is probable that double salts are not completely formed in solution, but only at the moment of crystallisation (compare p.). No resolution of a salt into acid and base by diffusion was observed in any of the experiments.

The several acids and bases exhibit the same order of diffusibility in all their compounds, the acid and basic radicals of the salts examined ranging themselves in the two following series, each beginning with the most diffusible; those among which the order has not been determined with certainty are grouped in brackets:

Negative: [Chlorine, bromine, iodine]; nitric acid; [chloric, perchloric, and permanganic acids]; fluorine; chromic acid; sulphuric acid; carbonic acid.

Positive: Hydrogen; [potassium, ammonium]; silver, sodium; [calcium, strontium, barium, lead, mercury]; [manganese, magnesium, zinc]; copper; aluminium.

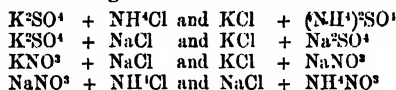
On the constitution of Salts in Solution as determined by their Thermic relations, see HEAT (pp. 978-987).

Solubility of Saline Mixtures (F. Rudorff, *Ber.* vi. 482, 643).—When water is saturated with two salts which exert no chemical action on one another (the same acid or base being common to both), the solubility of each is found to be diminished. For example, 100 c.c. water at 12° dissolve 29.1 grams of NH_4Cl and 173.8 grams of NH_4NO_3 together, whereas 100 c.c. water at the same temperature can dissolve 37.0 grams NH_4Cl , or 183.0 grams NH_4NO_3 singly. In some cases the proportion of each salt which dissolves is not influenced by the presence of a large excess of either

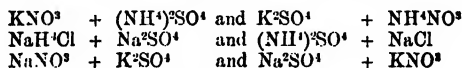
salt, but in other cases the presence of a large excess of one salt will almost prevent the solution of another. This is well illustrated by the behaviour of a saturated solution of the double salt, $(\text{NH}^4)_2\text{SO}^4 \cdot \text{CuSO}^4$. 10 grams of this solution contain at 16° , 0.855 gram of CuSO^4 and 0.712 of $(\text{NH}^4)_2\text{SO}^4$, but if one-fifth of its weight of CuSO^4 be dissolved in it by the aid of heat, the solution, when cold, contains 1.585 grams of CuSO^4 and only 0.565 of $(\text{NH}^4)_2\text{SO}^4$. If, on the other hand, one-fifth of $(\text{NH}^4)_2\text{SO}^4$ be dissolved by the aid of heat in 10 grams of this solution, and the whole be allowed to cool, the liquor will retain only 0.177 gram of CuSO^4 , but 1.816 of $(\text{NH}^4)_2\text{SO}^4$. If a larger amount of ammonium sulphate be employed, the quantity of copper sulphate remaining in solution may be still further reduced. 100 grams of water at 16.1° dissolve 76.2 grams CuCl^2 or 121.4 grams $\text{CuCl}^2 + 2\text{H}^2\text{O}$.

2. Rudorff has also endeavoured to ascertain whether a saturated solution of salts containing two bases and two acids is the same in whatever manner the bases and acids are combined; for instance, whether a saturated solution made from a mixture of KNO^3 and NH^4Cl is the same as one made from a mixture of KCl and NH^4NO^3 . The results obtained with a mixture of NH^4Cl and KNO^3 indicate that at 14.8° , 100 grams of water dissolve 38.8 grams NH^4Cl and 34.2 of KNO^3 , and, as might be expected, the addition of either of the pulverised salts to the solution causes no change of temperature. With mixtures of KCl and NH^4NO^3 , however, the results are found to vary with the proportions of the two salts in the mixture, and the addition of either of the salts to the solution causes a change of temperature; but the addition of KNO^3 or NH^4Cl produces no such effect. The addition of KCl or NH^4NO^3 to the saturated solution of NH^4Cl and KNO^3 , produces a change of temperature.

The following pairs of salts give a similar result:



But the pairs:



do not give saturated solutions of definite composition.

On the Double Decomposition and Thermic effects accompanying the dissolution of Mixed Salts, see *HEAT* (p. 979).

Decomposition of Salts by Water.—The action of water on mercuric sulphate, HgSO^4 , bismuth nitrate, $\text{Bi}^2\text{O}^3 \cdot 3\text{N}^2\text{O}^5 + 3\text{H}^2\text{O}$ and $\text{Bi}^2\text{O}^3 \cdot \text{N}^2\text{O}^5 + \text{H}^2\text{O}$, antimonious chloride, SbCl^3 , and potassio-calcic sulphate, $2\text{CaSO}^4 \cdot \text{K}^2\text{SO}^4 \cdot 3\text{H}^2\text{O}$, has been examined by A. Ditte (*Compt. rend.* lxxix. 915, 956, 1254). The decomposition of these salts takes place according to the same laws, resulting in the formation of a slightly soluble product, a basic salt, or calcium sulphate, while the water takes up free acid or potassium sulphate.

To each temperature there corresponds a liquid of such composition that any alteration of its concentration in one direction or the other is attended with decomposition, or reproduction of the original salt, and that, whatever may have been its original state, the liquid always returns to this limiting composition. The decomposition appears to be independent of the quantity of undecomposed salt remaining in the liquid, of the quantity of its undissolved constituents, or other acid or saline substances contained in the liquid, provided these bodies exert no chemical action on the salt or its constituents.

Crystallisation of Salts from Supersaturated Solutions.—Gernez showed some years ago that the crystallisation of a salt from a supersaturated solution is most readily induced by the introduction of a crystal of the same salt (v. 350), and J. M. Thomson has lately shown (*Chem. Soc. J.* xxv. 196) that the same effect is produced by con act with the crystal of a salt isomorphous with that which is contained in the solution. To produce this effect, however, mere identity of form between the introduced crystal or nucleus and the dissolved salt is not sufficient; the two must be truly isomorphous, that is to say, identical in chemical structure as well as in form. Thus, crystallisation is induced in a solution of magnesium sulphate, $\text{MgSO}^4 \cdot 7\text{H}^2\text{O}$, by the introduction of a crystal of the corresponding salts of zinc, nickel, cobalt, or iron, and a supersaturated solution of common alum may be made to crystallise suddenly by dropping into it a crystal of chrome-alum or iron-alum, but not by a cubic crystal of iron pyrites or an octohedral crystal of magnetic iron oxide.

In a mixture of two salts, not isomorphous, the introduction of a crystalline nucleus isomorphous with one of them may produce the following results: 1. Crystallisation may commence suddenly, spreading however gradually through the solution

and causing a deposition only of the salt isomorphous with the nucleus. 2. When sudden crystallisation takes place, causing the deposition of both salts, the salt isomorphous with the nucleus will preponderate. 3. The nucleus may remain growing slowly in the solution, and increasing by a deposition of the salt isomorphous with itself.

In a mixture of two isomorphous salts: 1. Sudden crystallisation may occur, producing a deposition of both salts, apparently in the proportion in which they exist in the solution. 2. When slow crystallisation takes place, the nucleus increases by deposition of the less soluble salt, showing that in mixed supersaturated solutions a gradation of phenomena may occur, passing from those shown in the crystallisation of a true supersaturated solution to those exhibited in the crystallisation of an ordinary saturated solution.

On crystallisation from Supersaturated Solutions, see also Tscherbatschew (*N. Petersb. Acad. Bull.* xix. 42); Violette (*Compt. rend.* lxxvi. 171); Mensbrugghe (*ibid.* lxxvi. 45, 713); de Coppet (*ibid.* 434); Gernez (*ibid.* 566); Tomlinson (*ibid.* lxxvi. 171; lxxviii. 194; lxxix. 167; *Ann. Chim. Phys.* [3], vi. 275); Marignac (*N. Arch. ph. nat.* xlviii. 120); Gernez (*Compt. rend.* lxxvi. 566; lxxix. 219, 1332; lxxx. 44; lxxxiv. 771, 1389); Lecoq de Boisbaudran (*ibid.* lxxx. 321, 393, 888); Grenfell (*Proc. Roy. Soc.* xxv. 124); Tomlinson (*ibid.* xxvi. 523; xxvii. 121). See also *Chem. Soc. J.* xxvi. 468-470; xxxi. 435, 436; xxxii. 696; *Jahresb. f. Chem.* 1873, 42-46; 1874, 42; 1875, 42-44; 1876, 48; 1877, 77-80; 1878, 57.

On the Dissociation-tensions of Hydrated Salts, see HEAT (pp. 1012, 1015).

On the Decomposition of Ammonium Salts in Aqueous Solution at low temperatures, see p. 1015.

On the Heat of Formation and Solution of Salts, see pp. 953-958, and 976-994.

SALVIOL. See SAGREOL (p. 1771).

SAMAITTE. See v. 187; also under GEHELENITE (p. 859 of this volume).

SAMARSKITE. Crystals of this mineral from Mitchell County, North Carolina, have been measured by E. S. Dana (*Sill. Am. J.* [3], xi. 201). It occurs, often imbedded in a decomposed felspar, in mica-slates, traversed by granitic veins. It is velvet-black, translucent with brownish colour on the edges, and is accompanied by an octohedrally crystalline mineral (microlite or pyrochlor), columbite and a yellow mica. The observed forms, $\infty P \infty$, $\infty \bar{P} \infty$, P , ∞P , $\infty \bar{P} 2$, $\bar{P} \infty$, $3\bar{P} 2$, may be referred to the axial ratio

$$a : b : c = 1.1883 : 0.949$$

giving by calculation the prismatic angle $122^\circ 46'$. Analysis (1) by Miss Ellen Swallow (*Sill. Am. J.* [2], xi. 201); (2) by O. D. Allen (*ibid.* [3], xiv. 128); (3) by J. L. Smith (*ibid.* xiii. 359); (4) by Rammelsberg (*Ann. Phys. Chem.* [2], ii. 658; *Jahrb. f. Min.* 1878, 529). Rammelsberg has also analysed samarskite from the Ural. No. 5 is the mean of four analyses:

	1	2	3	4	5
Nb ² O ⁵	54.96	37.20	55.13	41.07	55.34
Ta ² O ⁵	—	18.60	—	14.36	—
SiO ²	—	—	—	0.56	—
TiO ²	—	—	—	—	1.08
SnO ²	0.16	—	—	—	—
WO ³	—	0.08	0.31	0.16	0.22
Ce ² O ³	5.17	4.25	4.24	2.37	—
La ² O ³	—	—	—	—	4.33
Di ² O ³	—	—	—	trace	—
Y ² O ³	12.84	14.45	14.49	6.10	8.80
Er ² O ³	—	—	—	10.80	3.82
Fe ² O ³	—	—	—	14.61 ^(*)	14.30 ^(*)
FeO ³	14.02	10.90	11.74	—	—
MnO	0.91	0.75	1.53	—	—
UO ³	9.91	12.46	10.96	10.90	11.94
CaO	—	0.55	—	—	—
MgO	0.52	—	—	—	—
X ⁽¹⁾	0.66	1.12	0.72	—	—
Y ⁽²⁾	1.25	—	—	—	—
Specific gravity .	100.40	100.36	99.12	100.93	99.83
	—	—	—	5.839	5.672

(¹) Loss by ignition.

(²) Insoluble residuc.

(³) With Mn²O³.

Rammelsberg infers from these analyses that samarskite is a heminiobate (tantate), isomorphously mixed with a uranate; and as $U : (Nb, Ta) = 1.10$ (nearly), the formula of samarskite is $\left. \begin{matrix} 8R^4Nb^4O^{21} \\ R^4U^3O^{21} \end{matrix} \right\}$, or



New Metals in Samarskite.—Lecoq de Boisbaudran (*Compt. rend.* lxxxix. 212) observed that the solution of an oxide extracted from samarskite gave a pair of absorption-bands in the blue at 480° and 463.5° , and another pair in the violet at 417° and 400.75° . In both pairs, the most refrangible band is the narrower and more intense of the two. These bands are not identical with those of the decipium, recently described by Delafontaine, or of any other known substances, and indicate the existence of a new metal which Lecoq designates by the name *Samarium*. The bands 417° and 400.75° were observed some time ago by Soret (*Compt. rend.* 1878, lxxxvi. 878).

Delafontaine, in examining the earths obtained from samarskite, has observed appearances which lead him to suspect the existence of a new earth different from any yet described (*Ann. Chim. Phys.* [5], xiv. 238). See YTTRIUM-METALS.

SAMBUCUS. An analysis by J. Huber of the ash of elder-tree bark (*Sambucus nigra*) has been published by G. C. Wittstein. The air-dried bark lost at 110° , 11.666 per cent. water, and the bark dried at that temperature yielded 11.717 per cent. of ash having the following composition:

K ² O	Na ² O	CaO	MgO	Al ² O ³	Fe ² O ³	Cl	SO ³	P ² O ⁵	SiO ²	CO ²
13.96	0.97	30.92	10.73	0.25	0.35	0.18	5.82	8.04	5.46	23.27 = 99.95.

SANDAL-WOOD. An amorphous substance, having the composition $C^{17}H^{16}O^6$, is obtained from this wood, and more abundantly from Caliatour wood, by treatment with boiling alcohol and precipitation of the concentrated extract with water; it may be purified by converting the crude product into a lead-salt, washing this salt with hot alcohol, and decomposing it with sulphuric acid. The pure substance melts at 104° – 105° , dissolves in alcohol, acetic acid, alkaline carbonates, and caustic alkalis, and is precipitated from alkaline solutions by hydrochloric acid. When fused with potash, it yields resorcinol, acetic acid, and probably catechol and protocatechuic acid. By oxidation with potassium permanganate, it gives oxalic and acetic acids, together with a substance having the odour of vanillin. Reducing agents appear to have no action on this colouring matter. By the action of hydrochloric acid at 180° , it is decomposed into methyl chloride, a body soluble in hydrochloric acid, which crystallises in colourless needles, and forms a crystalline precipitate (m. p. 81°) with bromine-water; a substance soluble in alcohol, and having the composition $C^{11}H^{10}O^3$; and a black residue insoluble in alcohol, but soluble in caustic alkalis (Franchimont & Sicherer, *Ber.* xii. 14).

SANIDIN. On the variations in the crystallographic elements of this monoclinic felspar, see J. Strüver (*Zeitschr. f. Kryst.* i. 343; *Jahresb. f. Chem.* 1877, 1333).

SANTONIC ACID, $C^{15}H^{20}O^4$. The preparation and properties of this acid have been already described. For further details respecting its crystalline form and optical characters, see J. Strüver (*Gazz. chim. ital.* 1876, 349; *Jahresb. f. Chem.* 1876, 617).

By the action of hydriodic acid, santonin acid is converted into a hydrocarbon, $C^{15}H^{22}$, which is lighter than water, boils between 235° and 246° , and yields an iodine-derivative, $C^{15}H^{23}I$. By boiling for several days with hydriodic acid and amorphous phosphorus, santonin acid is converted into an isomeride of santonin, $C^{15}H^{18}O^3$ (also formed in like manner from santonin), which melts at 160.5° , and distils between 238° and 240° (Cannizzaro & Amato, *Gazz.* 1874, 446, 452).

Methyl santonate, $C^{15}H^{18}(CH^3O)^4$, is prepared by dissolving 1 mol. santonin acid and 4 mols. KHO in methyl alcohol, evaporating the solution to dryness, and heating the residue with methyl alcohol and excess of methyl iodide under a pressure of two atmospheres; or by the action of methyl iodide on a solution of sodium santonate in methyl alcohol under pressure. The unattacked methyl iodide and part of the alcohol having been distilled off, water is added, the methyl santonate extracted by agitation with ether, and the oily residue left on evaporating the ether is washed with water, and finally purified by crystallisation from ether and from methyl alcohol. Methyl santonate crystallises in colourless needles melting at 86° – 86.5° (Cannizzaro, *Gazz.* 1876, 355).

Ethyl santonate, $C^{15}H^{18}(C^2H^5O)^4$, obtained by heating silver santonate with excess of ethyl iodide, or by passing hydrogen chloride into an alcoholic solution of santonin

acid, crystallises in fine prisms melting at 88° – 89° . It is saponified by boiling for eighteen hours with soda-ley of the strength of 4 per cent. It dissolves slowly in cold nitric acid, and after the lapse of an hour or two is precipitated therefrom by water without alteration; but after twenty to thirty hours it is partly decomposed with separation of santonin acid (Sestini, *Gazz.* 1876, 148).

Acetyl-santonin acid, $C^{15}H^{10}(C^2H^3O)O^4$.—When santonin acid is heated for six hours with eight or ten times its weight of acetyl chloride in a flask placed in a water-bath and connected with a vertical condenser, and the product is afterwards distilled, there remains in the flask a dense fuming liquid, which may be freed from undecomposed acetyl chloride by passing a rapid stream of cold air through it for about sixteen hours. There then remains a yellowish-white, confusedly crystalline mass, which is to be well washed with cold water, drained, dried between bibulous paper, and digested three times in succession with a small quantity of ether, which dissolves a certain portion of it, leaving a white crystalline mass nearly insoluble in cold water, soluble in boiling alcohol and ether, slightly soluble in cold ether, very soluble in chloroform, melting at 139° – 140° . This substance is acetyl-santonin acid. By spontaneous evaporation of its solution in chloroform it may be obtained in large, hard, pointed prisms. The solution in boiling ether yields it, by cooling and evaporation, in small, very well formed, four and six-sided prisms terminated by pyramids with unequal faces. These crystals, like those of santonin acid itself, act strongly on polarised light. It appears to be the only product of the action of acetyl chloride on santonin acid.

Acetyl-santonin acid heated for two or three hours in boiling water is converted into acetic and santonin acids. If dilute alcohol is used instead of water, an ethylic ether is formed, which melts below 100° . The acid, heated in the dry state to 180° – 200° , is resolved into acetic acid and santonin anhydride (santonin), $C^{15}H^8(C^2H^3O)O^4 = C^2H^4O^2 + C^{13}H^8O^3$ (Sestini, *Gazz.* 1875, 121).

Santonin chloride, $C^{15}H^{10}O^3Cl$, is formed by heating santonin acid with phosphorus trichloride, and separates from solution in ether, in crystals which melt at 170° – 171° , and are decomposed by water and alcohol, yielding santonin acid and ethyl santonate respectively. The same compound is obtained by the action of acetyl chloride on santonin acid. Santonin bromide and iodide are produced in like manner by treating santonin acid with bromide or iodide of phosphorus. The iodide melts at 136° and the bromide at 145.5° (Cannizzaro a. Valente, *Gazz.* 1878, 309).

Hydrosantonin acid, $C^{15}H^{12}O^4$. The sodium salt of this acid is obtained by treating a solution of sodium santonate with sodium amalgam of 5 per cent., and the free acid may be precipitated from its solution by hydrochloric acid. The acid separates from ethereal solution in colourless crystals belonging to the orthorhombic system, melts and decomposes at 170° , is less soluble in alcohol and ether than santonin acid, and is optically dextrogyrate. The sodium salt, $C^{15}H^{12}NaO^4 \cdot 3H^2O$, forms orthorhombic crystals, which give off part of their water of crystallisation on exposure to the air. The crystals of the potassium salt contain $2H^2O$ (Cannizzaro, *Gazz.* 1876, 341).

Hydrosantoninide, $C^{15}H^{10}O^3$, is obtained by boiling a solution of hydrosantonin acid in glacial acetic acid for several hours, or better by heating the acid with glacial acetic acid in closed tubes at about 150° for four hours, and in either case distilling off the acetic acid till the temperature rises to 186° . It is a crystalline substance melting at 155° – 156° (Cannizzaro a. Valente, *Gazz.* 1878, 309).

Acetyl-hydrosantoninide, $C^{17}H^{20}O^4$, is formed by the action of acetyl chloride in excess on hydrosantonin acid:



It melts at 204° , and sublimes at a higher temperature. It is but slightly soluble in ether, and almost insoluble in water; is not decomposed by hot aqueous potash, but when heated with alcoholic ammonia at 130° , yields a substance having the composition of hydrosantoninamide.

Benzoyl-hydrosantoninide, $C^{22}H^{24}O^4 = C^{15}H^{10}(C^7H^5O)O^3$, prepared in a similar manner, crystallises in colourless needles melting at 157° . It closely resembles the acetyl-compound, but is decomposed by heating with aqueous potash.

Hydrosantoninamide (?), $C^{15}H^{12}NO^3$, is formed by heating acetyl- or benzoylhydrosantoninide with alcoholic ammonia at 120° – 130° , and may be purified by evaporating the product, washing the residue to remove acetamide and benzamide simultaneously produced, and crystallising from alcohol. It is soluble in alcohol, less soluble in ether, and only slightly soluble in boiling water; melts, with decomposition, at 190° .

ISOMERIDES OF SANTONIN ACID (Cannizzaro, *Gazz.* 1876, 341; Cannizzaro a. Valente, *ibid.* 1878, 309). The addition of the elements of water to santonin, $C^{15}H^8O^3$, gives rise to five isomeric acids, $C^{15}H^{10}O^4$, viz. a bibasic acid, *photosantonin*

acid, and four monobasic acids, viz. *santonin acid*, *santoninic acid* (already described, vii. 1076), *metasantonin acid*, and *parasantonin acid*. These four monobasic acids differ not only in their crystalline form, solubility, and other physical characters, but also in their behaviour to reagents; they are therefore metameric, not merely isomeric.

Metasantonin Acid is formed by abstraction of hydrogen from hydrosantonin acid. On adding silver nitrate to a solution of sodium hydrosantonate, a white precipitate of silver hydrosantonate is produced, which dissolves on heating, with precipitation of metallic silver; and on continuing the heat for half an hour, adding soda from time to time to keep the solution nearly neutral, and finally precipitating the silver oxide which remains in solution by adding an excess of alkali, a liquid is obtained which, when acidified with nitric acid, deposits metasantonin acid in the crystalline state; and a further quantity may be obtained from the solution by agitation with ether. Metasantonin acid may, however, be more conveniently prepared by distilling santonin acid under a diminished pressure of 52–43 mm., stopping the distillation as soon as the distillate becomes coloured, and the boiling point rises. Both the distillate and the residue in the retort are dissolved in a solution of sodium carbonate, and after agitation with ether to remove oily matters, the alkaline solution is precipitated with an acid, and the metasantonin acid purified by crystallisation from ether. Metasantonin acid is also formed by the action of alkaline solutions on santonide, $C^{15}H^{10}O^3$. Metasantonin acid, when purified by repeated crystallisation from ether, melts, with decomposition, at 160° – 161° . Its alkali-salts are very soluble. Its specific rotatory power is greater than that of santonin acid.

Metasantonin chloride, $C^{15}H^{10}O^3Cl$, prepared by the action of acetic chloride or of phosphorus trichloride on metasantonin acid, crystallises in slender needles melting at 139° , moderately soluble in ether. **Methyl metasantonite**, prepared by passing hydrochloric acid into a methyl-alcohol solution of metasantonin acid, forms large lustrous crystals melting at 101.5° – 102.5° .

Parasantonin Acid, $C^{15}H^{20}O^4$, is prepared from parasantonide (p. 1779) by boiling it with soda-solution, precipitating with an acid, and purifying by crystallisation from ether or from water. It may also be obtained by decomposing parasantonide with boiling dilute hydrochloric acid. The free acid forms large white crystals, which are moderately soluble in ether and in water. It is a strong acid, easily expelling carbonic acid from its salts. The parasantonates are mostly very soluble in water and in alcohol, but difficult to obtain in the crystalline state. The *barium salt*, $(C^{15}H^{10}O^4)^2Ba$, forms slender needles. Parasantonin acid, when treated with acetic chloride or phosphorus trichloride, does not yield the corresponding chloride, but is converted into parasantonide. **Methyl parasantonate** crystallises in hard prisms melting at 183° – 184° . **Ethyl parasantonate** forms colourless needles melting at 172° , only sparingly soluble in ether.

Photosantonin Acid. Sestini, in 1865 (*Repertorio ital. chim. pharm.* 1865), observed that when an alcoholic solution of santonin was exposed to direct sunlight, it was decomposed, with production of an amorphous resinous substance, a small quantity of formic acid, and a crystalline compound since ascertained to be the di-ethyl salt of photosantonin acid, $C^{15}H^{18}(C^2H^5)^2O^4$. If the alcohol is anhydrous, nothing but amorphous resinous compounds are obtained, but with aqueous alcohol, ethyl photosantonate is produced with comparatively little resin, 85 grams of santonin in 6 litres of alcohol of 65 per cent. having yielded 28 grams of the ether after being exposed to the summer sun for a month. On substituting methyl for ethyl alcohol, the corresponding methyl compound is produced. The ether is precipitated in the crystalline state on mixing the alcoholic solution with six to eight times its volume of a dilute solution of sodium carbonate, and may be purified by crystallising it first from alcohol, and then from ether-alcohol. Photosantonin acid is also formed when an aqueous solution of sodium santonate, or santonin, suspended in a solution of sodium carbonate, is exposed to sunshine. A similar transformation is effected by the insolation of a solution of santonin in glacial acetic acid of 95 per cent., this being, in fact, the most convenient method of obtaining free photosantonin acid. The free acid may also be obtained from the ether by saponification with a dilute solution of sodium hydrate, or with baryta-water.

Photosantonin acid, $C^{15}H^{20}O^4.H^2O$, crystallises from its alcoholic solution in colourless prisms belonging to the orthorhombic system. It is only slightly soluble in boiling water, but readily in alcohol, ether, and chloroform. It loses its water of crystallisation at 100° , and then melts at 153° .

Photosantonin acid decomposes the alkaline carbonates, with the aid of heat, but does not yield crystalline compounds. **Calcium photosantonate**, $(C^{15}H^{10}O^4)_2Ca + 4H^2O$, crystallises in white silky needles, soluble with difficulty in cold water. On heating

this salt with calcium hydrate, a dicalcic salt is obtained which is readily soluble in water, but may be precipitated in white amorphous flocks by addition of alcohol. *Barium photosantonate*, $C^{15}H^{18}BaO^4 + 2H^2O$, is a white amorphous substance precipitated by alcohol from its aqueous solution. *Silver photosantonate*, $C^{15}H^{18}Ag^2O^4 + 4H^2O$, is obtained as a white precipitate on adding silver nitrate to a solution of barium photosantonate. The *diethyl photosantonate*, obtained in the manner previously mentioned by exposing a solution of santonin in dilute alcohol to direct sunlight, is identical with that prepared synthetically by the action of ethyl iodide on silver photosantonate. It crystallises in large very thin plates, which melt at 67° – 68° . It is noteworthy that both this compound and ethyl santonate become liquid in contact with moderately dilute nitric acid. *Methyl photosantonate*, prepared by the insolation of santonin dissolved in methyl alcohol, crystallises in long prisms, which melt at $56^{\circ}5'$, and are readily soluble in alcohol or ether, and but little soluble in water. The methyl compound prepared synthetically from methyl iodide and silver photosantonate melts at 51° – 52° .

SANTONIN, $C^{15}H^{18}O^2$. *Reactions*.—When santonin is added, even in considerable quantity, to *antimony trichloride*, no coloration is produced till the trichloride is heated to incipient ebullition, when a very characteristic bluish olive-green tint makes its appearance (Watson Smith, *Ber.* xii. 1420).

When santonin is digested with strong *sulphuric acid*, and small quantities of ferric chloride are added, the faint red colour at first produced quickly changes to a very fine purple (D. Lindo, *Chem. News*, xxxvi. 222).

Isomerides. Four compounds are known isomeric with santonin :—

(1 and 2). On boiling santonin with hydriodic acid (b. p. 127°) and amorphous phosphorus, until hydrocarbons cease to be formed, removing these by distillation in a current of steam, concentrating the residue, and neutralising with sodium carbonate, a mixture of two isomerides of santonin is precipitated. This mixture may be purified by crystallisation from water and ether, and the crystals of the two isomerides separated mechanically. One of them, which crystallises in long flexible needles, consists of *metasantonin*, which melts at $160^{\circ}5'$, and boils at 238° – 240° (p. 1776), whilst the other, not previously described, crystallises in large hard prisms melting at 136° . Both these compounds are very stable, and have the same rotatory power; they are not sensibly acted on by acetic anhydride or chloride, or by phosphorus trichloride. They both yield monobrominated derivatives when treated with bromine; *monobromometasantonin* crystallises in silky needles, melting at 212° , whilst the corresponding brominated derivative of the other modification melts at 114° (Cannizzaro a. Carnellatti, *Gazz.* 1878, 318).

(3). *Santonide*. When a solution of santonin acid in glacial acetic acid is boiled for several hours, and the acid is then distilled off until the temperature rises to 180° , a residue is left, which solidifies on cooling to a viscous mass of the colour of amber. This residue is agitated with ether and an aqueous solution of sodium carbonate, the ethereal solution decanted and evaporated, and the santonide thus obtained is purified by repeated crystallisation from ether. *Santonide* melts at 127° – $127^{\circ}5'$. The quantity obtained forms but a small proportion of the product, the greater proportion consisting of unchanged santonin acid, which is dissolved by the alkaline solution.

(4). *Parasantonide* is prepared and purified in a similar manner, but the distillation is continued until the temperature rises to 260° . It melts at 110° – $110^{\circ}5'$. Both santonide and parasantonide are laevorotatory, but santonide is the more energetic of the two. *Parasantonide*, boiled with caustic soda-solution, is converted into parasantonin acid (p. 1778) (Cannizzaro a. Valente, *Gazz.* 1878, 309).

SANTONOL. This name is given to two phenolic bodies, $C^{20}H^{18}O^2$, one crystalline, the other liquid, obtained by treating santonin with zinc in a current of hydrogen (vii. 1076).

SAPONIN, $C^{32}H^{54}O^{18}$ (v. 192; vi. 1013). J. Christophsohn (*Arch. Pharm.* [3], vi. 432, 461) infers from comparative experiments that the roots of *Saponaria officinalis* and *Gypsophila Struthium*, the bark of *Quillaja*, and the seeds of *Agrostemma Githago* contain one and the same saponin, the pure preparations obtained from all these sources exhibiting, on elementary analysis, the same composition, and yielding, when decomposed by dilute acids, equal quantities of sapogenin and sugar. The differences hitherto found in the analyses of saponin from various sources must therefore be attributed to impurities in the preparations. Christophsohn also gives the results of quantitative estimations of saponin in various drugs, made either by the preparation of barium-saponin, or by determining the quantity of sapogenin obtained by decomposing saponin with hydrochloric acid. According to these determinations :

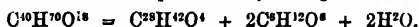
Quillaja bark contains	8.51- 8.83 p. c. saponin
Root of <i>Gypsophila Struthium</i>	14.52-14.80 "
Seed of <i>Agrostemma Githago</i>	6.54- 6.80 "
Root of <i>Saponaria rubra</i>	4.29- 5.61 "

Christophsohn also confirms the statement of Bolley and others (v. 194), that saponin and senegien (from senega-root) are identical.

Flückiger, on the other hand, is of opinion that several saponins may exist in different plants, probably forming a homologous series (*Arch. Pharm.* [3], x. 532).

Parillin, or **Sarsaparilla-saponin**, $C^{10}H^{70}O^{18} = C^{32}H^{124}O^{18}$ (saponin) + $8CH^2$ Flückiger (*loc. cit.*; also *Pharm. J. Trans.* [3], viii. 488) prepares this compound by digesting bruised sarsaparilla root several times with warm alcohol of sp. gr. 0.835, distilling the liquid to about one-sixth of the weight of the root employed, and mixing the thick extract with $1\frac{1}{2}$ times its weight of water. The glutinous parillin thereby separated is freed from the liquid by decantation, then suspended in water the liquid is filtered off, and the residue washed.

Parillin is less soluble in weak spirit than in strong alcohol or in water. From boiling alcohol—best from that of sp. gr. 0.970—it crystallises in double-refracting laminae or prisms, but never in measurable crystals. Air-dried parillin contains water of crystallisation which it gives off at 100° . It melts at 210° , is almost insoluble in cold water (1 pt. in 10,000), dissolves at 25° in 25 pts. alcohol of sp. gr. 0.814, much more freely in boiling alcohol. Chloroform dissolves it readily, and leaves it on evaporation in the form of a syrup, which, however, may be crystallised from water. Parillin does not excite sneezing, like saponin, and in the solid state does not taste harsh, but exhibits this taste in aqueous and more decidedly in alcoholic solution; it has a neutral reaction, and is inactive to polarised light. Strong sulphuric acid dissolves parillin with yellow colour, changing, by absorption of water, into a splendid red which lasts for days. Heated with sulphuric acid of 10 per cent., or with phosphoric acid, it assumes a green colour, changing to red and finally to brown, the reaction not being altered by addition of nitric acid or bromine. An aqueous solution of parillin gives with alcoholic, but not with aqueous lead acetate, a precipitate soluble in excess of lead acetate or of alcohol; it is also precipitated by basic lead acetate and by tannic acid. It does not reduce Fehling's solution at ordinary temperatures, and only after several hours when heated; neither does it reduce a cold solution of bismuth nitrate, or a solution of mercuric iodide in sodium bicarbonate. On boiling with dilute acids, however, reduction takes place, a sugar, at least partially crystallisable, being first produced, and a flocculent substance, insoluble in water, called parigenin, being afterwards separated. This sugar reduces all the solutions above mentioned. The reaction is represented by the equation:



This decomposition is accompanied by the production of an extremely sensitive green fluorescence, which is likewise produced when hydrogen chloride is passed into a solution of parillin in chloroform, and in the decomposition of parillin by sulphuric acid; it disappears on addition of water or ammonia.

Parigenin, $C^{28}H^{42}O^4$, is nearly allied to sapogenin, $C^{14}H^{22}O^2$, also to cyclamiretin, $C^{14}H^{22}O^3$, and, like the latter, is but slowly acted on by fused alkalis; it is, however, readily attacked by acetyl chloride (Flückiger).

SAPPHIRE. On the artificial formation of this gem, see **RUBY** (p. 1767).

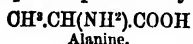
SARAWAKITE. A crystallised mineral, probably a chloride of antimony, occurring in cavities of antimony in the state of Sarawak, Borneo. The crystals appear to be quadratic; they are rounded on the edges, and have a diamond lustre (Frenzel, *Min. Mitth.* 1877, 300).

SARCINE. This base has been found, together with carnine, guanine, xanthine, and hypoxanthine, in the extract obtained by boiling yeast with water (Schutzenberger, *Compt. rend.* lxxviii. 493); also, together with guanine, in the spermatoc fluid of the salmon (Miescher, *Ber.* vii. 376).

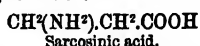
SARCOSINE, or **METHYL-GLYCOCINE**, $CH(CH^3)NH^2.COOH$. See **GLYCOCINE** (p. 879).

SARCOSINIC ACID, $C^3H^3NO^2 = CH^2(NH^2).CH^2.COOH$. An acid occurring, together with a red colouring matter, in a variety of shellac from Mexico, called 'Arré' by the Indians, and known in commerce as *Soma de Sonora* or *Gummi Sonora*. It crystallises in white silky scales, dissolves easily in cold, still more readily in hot water, but is insoluble in absolute alcohol and in ether; the aqueous solution has an acid reaction. It melts at 195° , does not sublime, gives off ammonia when ignited

with soda-lime, but not when boiled with caustic soda. Treated in aqueous solution with nitrous acid, it gives off nitrogen and is converted into lactic acid. It is a weak mono-basic acid; its silver and sodium salts are crystalline; the barium and calcium salts amorphous. It forms crystalline compounds with hydrochloric and nitric acids, and is carbonised by heating with strong sulphuric acid. It is isomeric with alanine, sarcosine, lactamide, and urethane, and agrees in many of its characters with alanine, being like the latter an amido-acid, but differs from it in taste and crystalline form, and in possessing a much less decided acid character. The difference between the two may perhaps be represented by the following formulæ:



Alanine.



Sarcosinic acid.

SASSAFRAS OIL. Rectified sassafras oil, when cooled to 0° , deposits a considerable quantity of crystals, only a small portion remaining fluid. The oil obtained by heating the crystals to 70° solidifies only after exposure for several weeks to a temperature below 0° ; but if the crystals be allowed to melt at a temperature not exceeding 20° , the liquid mass solidifies easily on cooling. These characters demonstrate the identity of St. Evre's sassafras camphor (v. 199) with the safrol of Grimaux a. Ruotte (vi. 1014). The crystals of safrol belong to the monoclinic system (Arzruni, *N. Rep. Pharm.* xxv. 615).

SAUSSURITE (v. 200). This mineral has been found in thin layers and irregular masses in the nephrite of the Künlün range in Central Asia (p. 1387). An analysis by v. Fellenberg (*Münch. Akad. Ber.* iii. 227) gave:

SiO^2	Al^2O^3	Fe^2O^3	CaO	MgO	K^2O	H^2O
48.25	22.60	7.47	1.03	12.70	1.80	6.22

leading to the formula $(\text{CaO}, \text{K}^2\text{O})3\text{SiO}^2 + 2(\text{Al}^2\text{O}^3, \text{Fe}^2\text{O}^3).3\text{SiO}^2$, in which $\text{K}^2\text{O} : \text{CaO} = 1 : 2$ and $\text{Al}^2\text{O}^3 : \text{Fe}^2\text{O}^3 = 5 : 1$.

SAYNITE. The mineral hitherto known by this name, or by that of nickel-bismuth glance (i. 596), is essentially a mixture of polydimite (p. 1660) with bismuth-glance (Laspeyres, *J. pr. Chem.* [2], xiv. 397).

SCAMMONY. For the preparation of pure scammony-resin, E. Perret (*Bull. Soc. Chim.* [2], xxviii. 522) recommends exhausting the crude commercial resin with boiling alcohol, neutralising the alkaline filtrate with dilute sulphuric acid, and separating the resulting precipitate, which contains all the colouring matter, by filtration. The filtrate, freed from alcohol by distillation and dried by prolonged heating at 104° , yields the pure anhydrous resin.

SCANDIUM. A metal of the yttrium group, discovered by F. Nilson in 1879, and further examined by Cleve. It occurs in gadolinite and yttritanite, has the atomic weight 44, and forms only one oxide, Sc^2O^3 (see YTTRIUM METALS).

SCAPOLITE. F. D. Adams (*Sill. Am. J.* [3], xvii. 315) finds that many scapolites contain chlorine, fourteen specimens from different localities yielding that element in quantities varying from a mere trace to 2.4 per cent. In some cases the chlorine was not driven off, even at a white heat. It is probable that when the scapolite decomposes, the chlorine is one of the first constituents to disappear.

SCHÉELITE. See TUNGSTATES.

SCHIZOMYCETES. See FERMENTATION and FERMENTS (pp. 776, 782).

SCHRÖCKINGERITE. A mineral from Joachimsthal, containing uranic oxide, carbonic acid, and water, together with a small quantity of lime, and extremely small traces of sulphuric acid. Loss by ignition = 36.7 per cent. It forms spherical groups of light greenish-yellow six-sided tablets implanted on pitchblende. From its optical characters it appears to belong to the orthorhombic system (A. Schrauf, *Jahrb. f. Min.* 1873, 646).

SCLERETHRYTHRIN, SCLEROMUCIN, SCLEROTIC ACID, SCLEROCRYSTALLIN, and SCLEROKANTHIN. Constituents of ergot (p. 737); further, Dragendorff a. Podwissotzky (*Russ. Zeitschr. Pharm.* xvi. 129, 161; *Jahresb. f. Chem.* 1877, 943).

SCOLECITE. On the variety of scolecite occurring at Poonah in Hindostan, see POONAHLITE (p. 1663).

SCOPOLIA. *Scopolia japonica* is a solanaceous plant intermediate in character between *Scopolia* and *Atropa*. Its roots are used in Japan for the same purpose as *Atropa Belladonna* in Europe, but their effect is less powerful. They contain solanine, but no atropine. The plant is highly fluorescent.

SCORODITE. Crystals of this mineral from Dornbach in Nassau have been examined by G. vom Rath (*Jahrb. f. Min.* 1876, 394), who finds the axial ratio to be

$$a : b : c = 0.86730 : 1 : 0.95580$$

and for the angles of the primary pyramid:

Macrodiagonal terminal edge	=	102° 52'
Brachydiagonal	"	114° 40'
Lateral edge	"	111° 6'

Brazilian scorodite, measured by N. v. Kokscharow (*ibid.* 1877, 800), gave values agreeing exactly with the above.

W. v. Beck (*ibid.* 162) has analysed a dark liver-coloured or indigo-blue mass of sp. gr. 3.084, occurring on a newly-discovered bed of silver ore in the Troitzker Circle of the Government of Orenburg, and regards it as a mixture of scorodite with brown iron ore and silver chlorobromide. The results are given in the following table. 1-3. Analyses. 4-6. The same, after deduction of silver-compounds and lime:

	AgCl, AgBr (%)	CaO	Fe ² O ³	As ² O ³	H ² O
1. (found)	5.78	2.18	36.80	42.37	13.43 = 100.56
2. "	6.41	2.07	36.73	41.44	13.43 = 100.08
3. "	9.25	1.48	35.40	40.44 (?)	13.43 = 100
4. (corr.)	—	—	39.75	45.75	14.50 = 100
5. "	—	—	40.10	45.24	14.66 = 100
6. "	—	—	39.66	45.30	15.04 = 100

(%) Enclosing small quantities of matrix. (?) Determined by difference.

On so-called *earthy scorodite* from Nertschinsk, see JOGYNITE (p. 1142).

SEBIC, or SEBACIC ACID, C¹⁰H¹⁸O⁴ (v. 212). O. N. Witt (*Ber.* vii. 219) prepares this acid by mixing castor-oil with the strongest soda-ley, leaving the mixture for some hours at 40°, separating the resulting hard crust from the small remaining quantity of liquid; then crushes, dries, and heats it, with stirring, in an iron vessel till the smell of octyl alcohol is no longer perceptible and the mass begins to turn brown; and immediately shakes the residue into cold water. From the solution thus obtained, the sebic acid may be precipitated by hydrochloric acid. See also Neison (*Chem. Soc. J.* xxvii. 301).

Metallic Sebatates. Sebic acid is bibasic. Its normal salts appear to be more stable than the acid salts, the latter being, in some instances, decomposed by prolonged boiling of their acid solutions. The acid salts appear to be all more or less soluble in water; the normal salts of the heavy metals and of calcium are insoluble in water; the rest are soluble.

Potassium salts, C¹⁰H¹⁶O⁴KH, is prepared by adding a hot alcoholic solution of potassium hydrate to a hot alcoholic solution of sebic acid keeping the latter in excess, and separates at once in minute crystals which are easily purified by washing with alcohol. It forms white anhydrous microscopic needles, not deliquescent, easily soluble in cold, still more readily in hot water, moderately soluble in alcohol, yielding strongly acid solutions. C¹⁰H¹⁴O⁴K², obtained by adding a hot alcoholic solution of sebic acid to a large excess of alcoholic potash, and purified by boiling with alcohol, washing with hot alcohol and drying, is a white anhydrous crystalline powder, consisting of minute granules, readily soluble in cold, still more in hot water, sparingly in alcohol, forming solutions which are neutral to litmus.

The *sebatates of sodium* are prepared in the same manner as the potassium salts. C¹⁰H¹⁴O⁴NaH is a fine crystalline powder, easily soluble in water, moderately in alcohol, forming solutions which have a marked acid reaction. C¹⁰H¹²O⁴Na² is obtained in very fine microscopic crystals, non-deliquescent, very soluble in water, slightly soluble in alcohol.

Ammonium sebatates can be obtained in solution in the same manner as the potassium salts, but on attempting to separate them in the solid state, they are invariably decomposed with loss of ammonia.

Silver sebate, C¹⁰H¹⁰O⁴Ag², obtained by precipitation, is a white powder rapidly turning pink on exposure to light, and readily soluble in nitric acid.

Barium salts, (C¹⁰H¹⁰O⁴)²BaH², prepared by boiling barium carbonate with excess of aqueous sebic acid, is a white confusedly crystallised non-deliquescent salt, easily soluble in water, and crystallising therefrom in needles. C¹⁰H¹⁰O⁴Ba, prepared by prolonged boiling of the acid with excess of barium carbonate, separates from concentrated solutions in white anhydrous crystalline crusts, easily soluble in water with neutral reaction. The *strontium salts* were prepared in like manner. The *acid*

salt forms white crystalline crusts; the *normal salt*, a white anhydrous crystalline powder. *Calcium salts*, $(C^{10}H^{16}O^4)^2CaH^2$, prepared by adding a hot solution of acid potassium sebate to a solution of calcium chloride, is a dense white precipitate, slightly soluble with acid reaction in water, partially decomposed by prolonged boiling into sebic acid and the normal salt. $C^{10}H^{16}O^4Ca$, obtained by adding normal sodium sebate to calcium chloride solution, is a dense white amorphous precipitate.

Magnesium salts, $(C^{10}H^{16}O^4)^2MgH^2$, prepared like the acid barium salt, crystallises in groups of white anhydrous needles, easily soluble in water with strong acid reaction, very slightly soluble in alcohol. $C^{10}H^{16}O^4Mg$, prepared like the normal barium salt, forms thin white crystalline crusts readily soluble in water, slightly in alcohol.

Zinc sebate, $C^{10}H^{16}O^4Zn$, is a heavy white pulverulent precipitate, slightly soluble in water and in dilute ammonia. *Nickel sebate*, $C^{10}H^{16}O^4Ni$, obtained by dissolving nickel hydrate in aqueous sebic acid, forms pale green anhydrous crystalline crusts, slightly soluble in cold, more soluble in hot water, insoluble in alcohol. *Cobalt sebate*, $C^{10}H^{16}O^4Co$, prepared in like manner, forms thin purple-blue anhydrous scales slightly soluble in cold, somewhat more in hot water. Solutions of nickel and cobalt salts are not precipitated by sebic acid or its alkali-salts (Neison). According to O. N. Witt (*loc. cit.*), the rose-coloured solution of cobalt carbonate in boiling aqueous sebic acid, if evaporated after the excess of acid has separated out on cooling, yields crystalline crusts of the hydrated salt $C^{10}H^{16}O^4Co + 2H^2O$; and the same hydrate is obtained, by spontaneous evaporation, partly in rose-red granules made up of microscopic needles, partly in ruby-red prismatic crystals. It gives off the greater part of its water at 120° , assuming a splendid violet colour, the rest with slight decomposition at a higher temperature.

Lead sebate, obtained by precipitation, is a heavy white powder insoluble in water and alcohol, either hot or cold, not changed by boiling with sebic acid.

Cupric sebate, $C^{10}H^{16}O^4Cu$, is a light emerald-green bulky precipitate which shrinks considerably on drying and then forms a green light powder. It dissolves readily in ammonia, forming a dark purple solution, which leaves, on spontaneous evaporation, a bluish-green mass containing ammonia, possibly a cuprammonium sebate.

Mercuric sebate, $C^{10}H^{16}O^4Hg$, obtained by decomposing mercuric chloride either with normal or with acid potassium sebate, is a white insoluble precipitate. Sebic acid in hot aqueous solution does not precipitate mercuric chloride.

Mercurous sebate, $C^{10}H^{16}O^4Hg^2$, obtained by precipitating mercurous nitrate with potassium sebate, is a heavy white amorphous powder, slightly soluble in water, very slightly in alcohol.

Aluminium-hydrogen sebate, $(C^{10}H^{16}O^4)^3AlH^3$, obtained by precipitating a strong solution of alum with acid potassium sebate, or by boiling freshly precipitated alumina with excess of sebic acid, is a white friable powder, slightly soluble in cold, easily in hot water, and separating on cooling in white anhydrous semicrystalline scales (Neison).

Sebic Ethers (Neison, *Chem. Soc. J.* xxix. 314). *Methyl sebate*, $C^{10}H^{16}O^4(CH^3)^2$, is prepared by dissolving 2 pts. by weight of sebic acid in 1 pt. of warm methyl alcohol; gradually adding a double volume of strong sulphuric acid, and heating the mixture for some time on the water-bath, with frequent agitation; adding water after cooling; washing the oily layer thoroughly with water; dissolving it in ether; drying the ethereal solution over calcium chloride and potassium carbonate; distilling; heating the residue for some time at 120° , and leaving it to cool. The crude ether is thus obtained as a white waxy mass, which may be purified by boiling it with a very dilute solution of sodium carbonate, redissolving it in ether, distilling off the latter, and heating the residue at 150° . Methyl sebate thus prepared is a white wax having a strong and rather pleasant odour, and obtainable by spontaneous evaporation of its ethereal solution in small needles or plates having a nacreous lustre. Ether and hot alcohol dissolve it readily; cold alcohol slowly, but in considerable quantity. It is insoluble in cold water, slightly soluble in hot water. It is easily saponified by alkaline hydrates, but not by alkaline carbonates. It melts at 38° ; becomes hard and brittle at -25° to -30° ; and boils, though not without decomposition, at about 288° , yielding a brown distillate, which, however, may be decolorised by boiling its alcoholic solution with animal charcoal.

Ethyl sebate, $C^{10}H^{16}O^4(C^2H^5)^2$, is prepared by passing hydrochloric acid gas into an alcoholic solution of sebic acid, and purified by boiling it first with water, next with dilute sodium carbonate, and again with water; then dissolving it in ether, drying the ethereal solution over calcium chloride and potassium carbonate, distilling

off the ether, and submitting the residue to fractional distillation, collecting apart the portion (about 90 p. c.) which passes over between 306° and 310° .

Pure ethyl sebate is a colourless oily liquid having a density of 0.965 at 16° , and a strong odour like that of melons. It solidifies at -4.5° to a white wax consisting of nodules of minute needles and plates, and becomes hard and friable at -30° to -35° ; boils without decomposition at 307° – 308° . In its relation to solvents and to alkalis, it resembles the methylic ether.

Ethyl-hydrogen sebate is formed in small quantity in the preparation of the normal ether, but has not yet been obtained pure. It dissolves when boiled with sodium carbonate or shaken up with cold soda-ley, but a considerable portion is at the same time decomposed. On adding an acid to the resulting solution, the acid ether separates, together with small quantities of sebic acid and the normal ether, as an oil which readily crystallises at 10° in delicate snow-white needles.

Amyl sebate, $C^{10}H^{16}O_4(C^2H^{11})_2$, prepared like the ethyl-compound, forms, after purification, a colourless oil having a very strong but pleasant fruity odour, and a density of 0.9510 at 18° . When heated it becomes quite colourless, and when cooled to -5° partly solidifies in thin needles which increase in quantity on further cooling, but the greater portion still remains fluid at -35° . The needles disappear on raising the temperature to $+10^{\circ}$, and immediately on addition of a trace of water. This ether boils at a temperature above 360° . It is insoluble in water, but dissolves readily in alcohol either hot or cold, and in unlimited quantity in ether. It is not attacked by boiling solutions of alkaline carbonates or by cold solutions of alkaline hydrates, but is decomposed by alcoholic solutions of the latter, even at ordinary temperatures. When a dilute alcoholic solution of sodium hydrate is allowed to act slowly on an excess of normal amyl sebate, a considerable quantity of the *acid ether* $C^{10}H^{17}O_4(C^2H^3)$ is formed. The resulting solution, when left to evaporate, deposits sodium sebate, then, on addition of water, the undecomposed portion of the normal ether, whilst the sodium salt of the acid ether remains dissolved, and may be obtained by evaporation as a white very deliquescent mass, which may be purified by repeated treatment with alcohol and water. By carefully decomposing this salt with acetic acid, the acid amyl sebate is obtained as a yellowish oil, which solidifies at 10° to a white crystalline mass, easily soluble in alcohol, ether, and hot water, slightly in cold water, and splitting up at 325° into sebic acid and the normal ether.

Aniline-derivatives. Equal weights of sebic acid and aniline, heated together at 150° , produce: (1). *Sebanilide*, a neutral compound soluble in boiling alcohol. (2). *Sebanilic acid*, a monobasic acid, soluble in alcohol and ether (E. Maillot, *Compt. rend.* lxxxvii. 737).

SEEBACHITE. See PHACOLITE (p. 1513).

SELENIUM. *Occurrence and Extraction.*—According to Rössler a. Debray (*Zeitschr. anal. Chem.* 1877, 363), selenium is present in refined silver, being derived from the sulphuric acid (made from pyrites) used in the refining process. If the amount exceeds 1 pt. in 1000, the silver becomes unworkable.

From the seleniferous deposit, or mud, of the lead chambers in sulphuric acid works, the selenium may be advantageously extracted by dissolving it out with potassium cyanide. The washed mud is digested with a moderately strong solution of the cyanide at 80° – 100° till the red colour just changes to a pure grey; the residuo is lixiviated with boiling water till the liquid no longer shows a reddish opalescence on addition of hydrochloric acid; the solution is then filtered, and the selenium precipitated by hydrochloric acid. By this process, 1 pt. of selenium is obtained for every 2 pts. of potassium cyanide employed. The precipitated selenium contains only small quantities of copper and iron, and perhaps traces of mercury; it may be freed from these impurities by converting it into selenious oxide, subliming this compound, and precipitating the selenium with sulphurous acid (Petersson, *Ber.* vi. 1466; Nilson, *ibid.* vii. 1719).

On the occurrence of Selenium in Tellurium ores, see TELLURIUM.

Atomic Weight.—Petersson a. Ekmann, by reducing a known weight of selenious oxide, SeO_2 , with sulphurous acid, and weighing the reduced selenium, have found, as a mean of five experiments, that the atomic weight of selenium is 79.08 (*Bull. Soc. Chim.* [2], xxvii. 205).

Allotropic Modifications.—Observations on the allotropic modifications of selenium, especially the amorphous vitreous variety, and the granular or so-called metallic selenium, produced therefrom by fusion and slow cooling, have been made by Draper a. Moss (*Chem. News*, xxxiii. 1). Vitreous selenium has no definite melting point, but becomes softer at 60° and upwards, and perfectly fluid at 250° ; it is restored to

its original state by rapid cooling, and then remains unaltered at ordinary temperatures for years. Carbon bisulphide dissolves only traces of this modification. Thin splinters of it transmit light of ruby-red colour. When heated for some time between 94° and 200°, and then slowly cooled, it acquires a metallic aspect and granular fracture, and becomes perfectly opaque even in the thinnest layers. It melts at 217°, without previous softening, is perfectly fluid at 250°, and is reconverted into the vitreous modification by rapid cooling.

On the Electric Conductivity of the several Modifications of Selenium, see ELECTRICITY (p. 721).

Selenium enclosed in the vacuum of a Sprengel mercury-pump, or dipped into mercury, condenses the vapour of that metal, and becomes coated with a layer of substance which conducts electricity, and though merely superficial, cannot be removed either by mechanical or by chemical means, and therefore does not appear to consist of metallic mercury (R. J. Moss, *Chem. News*, xxxiii. 203).

Selenium imparts a greyish-blue colour to the flame of hydrogen (Fresenius, *Zeitschr. anal. Chem.* 1876, 295).

When selenium is dissolved in strong sulphuric acid, it is partly oxidised, and on boiling the green solution, it immediately becomes colourless, gives off large quantities of sulphur dioxide, and no longer yields a precipitate of selenium when mixed with water, but deposits red selenium on addition of stannous chloride. A highly concentrated solution of selenium in sulphuric acid, which has a blackish-green colour, does not readily give off sulphur dioxide, but this gas is immediately evolved on addition of fresh quantities of strong sulphuric acid (A. Hilger, *Ber.* vii. 26).

Selenious Oxide, Acid, and Salts. Selenious oxide absorbs dry hydrogen chloride rapidly and with considerable rise of temperature. The product first formed is an amber-yellow liquid composed of equal numbers of molecules of the two constituents ($\text{SeO}_2 \cdot \text{HCl}$). This liquid, when heated, begins to give off hydrogen chloride at 26°. Its dissociation-tension in millimeters at various temperatures is as follows:

Temperature . . .	30°	40°	55°	75°	100°	106°	118°
Tension . . .	15	48	142	313	664	760	1012

At low temperatures the liquid continues to absorb hydrogen chloride, and ultimately becomes converted into a transparent yellow crystalline solid, containing 2 mols. of hydrogen chloride to 1 of selenious anhydride ($\text{SeO}_2 \cdot 2\text{HCl}$). This substance is resolved by heat (its dissociation-tension being considerable even at the ordinary temperature) into hydrogen chloride and the compound $\text{SeO}_2 \cdot \text{HCl}$, which latter is permanent below 26°. The following tensions in millimeters were observed:

Temperature . . .	-20°	0°	12°	15°	22.5°	30°	33°
Tension . . .	60	219	418	483	672	760	993

Dry hydrogen bromide is rapidly absorbed by selenious anhydride, forming in the first place the compound $\text{SeO}_2 \cdot 2\text{HBr}$, which crystallises in brilliant steel-grey spangles. This compound is stable below 55°, but is resolved at higher temperatures into selenium, bromine, and water. Its solution in a very small quantity of water is nearly black; a large quantity decomposes it, forming hydrobromic and selenious acids. The compound $\text{SeO}_2 \cdot 2\text{HBr}$ energetically absorbs hydrobromic acid gas, with evolution of heat, giving rise to a crystalline compound corresponding with the formula $2\text{SeO}_2 \cdot 5\text{HBr}$. This compound is decomposed at 65° with formation of water and disengagement of bromine, but at lower temperatures it is transformed into $\text{SeO}_2 \cdot 2\text{HBr}$ and hydrobromic acid. The following are the values of the dissociation-tension of the compound $2\text{SeO}_2 \cdot 5\text{HBr}$ at various temperatures:

At -25° . . .	0 mm.	At 30° . . .	287 mm.
" - 6° . . .	108 "	" 41° . . .	335 "
" 0° . . .	135 "	" 54° . . .	404 " Traces of bromine
" + 11° . . .	191 "	" 62° . . .	404 " vapour.
" 14° . . .	209 "	" 70° . . .	Decomposition with abundant evolution of bromine.

Hydriodic acid reacts with selenious oxide even at -10°, the products being water, iodine, and selenium. Selenious oxide also combines with anhydrous *hydrocyanic* and *hydrofluoric acids*. Selenious oxide and *hydrogen selenide* in presence of water decompose each other, with separation of selenium. This result is always the same, whether the solutions be concentrated or dilute, hot or cold; and no compound corresponding with pentathionic acid has been obtained. The reaction affords a convenient

means of obtaining selenium soluble in sulphide of carbon (A. Ditte, *Compt. rend.* lxxxiii. 56, 223).

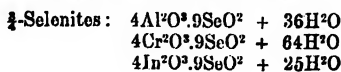
Selenious acid in presence of ammonium chloride is completely precipitated, by a *magnesium salt and ammonia*, after long standing or on brisk agitation, the precipitate of ammonium-magnesium selenite being crystalline, and exhibiting under the microscope a very close resemblance to that of ammonium-magnesium phosphate. This reaction affords the means of separating selenious acid from selenic, sulphurous, sulphuric, and telluric acids (Hilger a. v. Gerichsen, *Zeitschr. anal. Chem.* 1874, 132).

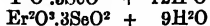
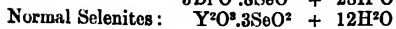
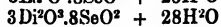
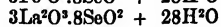
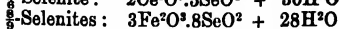
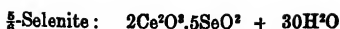
Selenites.—An elaborate investigation of these salts has been made by L. F. Nilson (*Researches on the Salts of Selenious acid*, Nova acta reg. Soc. Scient. Upsal. Ser. iii. 1875; *Bull. Soc. Chim.* [2], xxi. 258; xxiii. 260, 353, 494). The following is a summary of the results:

$\text{SeO}^3\text{K}^2 + x\text{H}^2\text{O}$	Very deliquescent prisms.
SeO^3KH	Very hygroscopic prisms.
$\text{SeO}^3\text{KH} + \text{SeO}^3\text{H}^2$	Shining prisms, permanent in the air.
$\text{SeO}^3\text{Na}^2 + 5\text{H}^2\text{O}$	Small needles, or large four-sided prisms.
SeO^3Na^2	Tetragonal prisms, formed by slow evaporation at 60° .
SeO^3NaH	Radiate prisms, permanent in the air.
$\text{SeO}^3\text{NaH} + \text{SeO}^3\text{H}^2$	Large prisms, permanent in the air.
$\text{SeO}^3\text{Li}^2 + \text{H}^2\text{O}$	Needles having a silky lustre.
SeO^3LiH	Prisms resembling arragonite.
$\text{SeO}^3\text{LiH} + \text{SeO}^3\text{H}^2$	Long prisms permanent in the air.
$\text{SeO}^3(\text{NH}^4)^2 + \text{H}^2\text{O}$	Formed by saturating an alcoholic solution of SeO^3H^2 with NH^3 . Small prisms, giving off 18 per cent. NH^3 on exposure to the air.
$2\text{SeO}^3(\text{NH}^4)^2 + \text{SeO}^3\text{H}^2$	By saturating an aqueous solution of SeO^3H^2 with NH^3 . Long deliquescent prisms.
$\text{SeO}^3\text{Ba} + \text{H}^2\text{O}$	Microscopic prisms.
$\text{SeO}^3\text{Ba} + \text{SeO}^2$	Sparingly soluble prisms, separating from a solution of BaCO^3 in SeO^3H^2 , on evaporation at 60° .
$\text{SeO}^3\text{Sr} + 3\text{H}^2\text{O}$	Crystalline powder.
$\text{SeO}^3\text{Sr} + \text{SeO}^3\text{H}^2$	Large shining prisms.
$\text{SeO}^3\text{Ca} + 2\text{H}^2\text{O}$	Small crystals having a satiny lustre; efflorescing in the air.
$\text{SeO}^3\text{Ca} + \text{SeO}^2$	Large crystals, forming on evaporation at 60° .
$\text{SeO}^3\text{Ca} + \text{SeO}^3\text{H}^2 + \text{H}^2\text{O}$	Shining prisms, obtained by evaporation at ordinary temperatures.
$\text{SeO}^3\text{Mg} + 6\text{H}^2\text{O}$	Hexagonal plates or short prisms, giving off $5\text{H}^2\text{O}$ at 100° .
$\text{SeO}^3\text{Mg} + \text{SeO}^3\text{H}^2 + 3\text{H}^2\text{O}$	Crystalline mass.
$\text{SeO}^3\text{Mn} + 2\text{H}^2\text{O}$	Amorphous precipitate, gradually becoming crystalline.
$\text{SeO}^3\text{Ni} + 2\text{H}^2\text{O}$	Crystalline powder.
$\text{SeO}^3\text{Ni} + \text{SO}^3\text{H}^2 + 2\text{H}^2\text{O}$	Four-sided prisms.
$\text{SeO}^3\text{Ni} + \text{SO}^3\text{H}^2 + \text{SeO}^2$	Small plates.
$\text{SeO}^3\text{Co} + 2\text{H}^2\text{O}$	Amorphous bluish-red precipitate.
$\text{SeO}^3\text{Co} + \text{SeO}^2$	Small red prisms.
SeO^3Cd	Small insoluble prisms.
$\text{SeO}^3\text{Cu} + 2\text{H}^2\text{O}$	Small bluish prisms.
$\text{SeO}^3\text{Cu} + \text{SeO}^3\text{H}^2 + 2\text{H}^2\text{O}$	Bluish-green powder.
$5\text{BeO} \cdot 2\text{SeO}^2 + 10\text{H}^2\text{O}$	
$\text{BeO} \cdot \text{SeO}^2 + 2\text{H}^2\text{O}$	
$\text{BeO} \cdot \text{SeO}^2 + \text{SeO}^3\text{H}^2$	
$\text{BeO} \cdot \text{SeO}^2 + 2\text{SeO}^3\text{H}^2$	

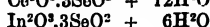
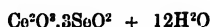
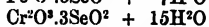
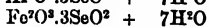
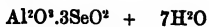
The gadolinite and cerite metals form selenites analogous in composition to those of aluminium, iron, indium, and chromium. The following selenites of these metals have been obtained:

1. From dilute solution of a normal salt and normal sodium selenite:



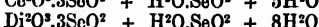
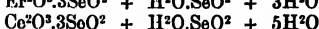
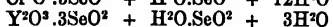
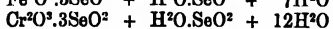


2. From basic salts with a quantity of acid exactly sufficient for the formation of normal salt:

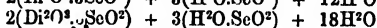
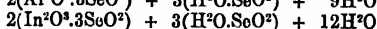
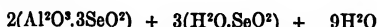


3. From basic or neutral salts with a quantity of acid sufficient for the formation of a diselenite:

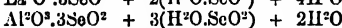
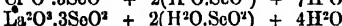
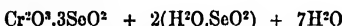
$\frac{4}{3}$ -Selenites:



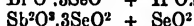
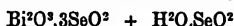
4. From a basic salt with a quantity of acid sufficient for the formation of a diselenite or of a tetraselenite:



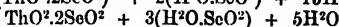
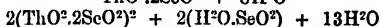
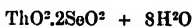
5. From a basic salt with a quantity of acid exactly sufficient for the formation of a tetraselenite:



Nilson has also obtained two selenites of bismuth and antimony, which exhibit a certain analogy between these trivalent metals and the preceding:



Among the rare earth-metals, thorium exhibits no analogy to the rest, not even with tin or zirconium, but stands alone with respect to its selenites, as in many other respects; thus:



Selenic Acid, SeO^4H^2 . v. Gerichten (*Liebig's Annalen*, clxviii. 214) prepares this acid from selenium containing sulphur by oxidising the selenium with nitric acid, adding potash, passing chlorine into the solution till it no longer gives a red precipitate with stannous chloride, then precipitating the selenic acid as barium selenate, and decomposing this salt with a slight excess of potassium carbonate. Any barium sulphate that may have been precipitated with it then remains undecomposed. This mode of separation is not exact enough for quantitative analysis, but sufficiently so for the purpose in hand. Any small quantity of barium selenate that may be dissolved may be recovered by slight concentration of the filtrate.

Selenic acid may be estimated by boiling it with hydrochloric acid, and determining the quantity of evolved chlorine by titration with iodine and sulphurous acid (Petersson, *Zeitschr. anal. Chem.* 1873, 287).

Selenic Oxide or Anhydride, SeO^2 .—By passing dry oxygen over dry selenium heated in a glass tube, and then passing the resulting selenious oxide, together with oxygen, over red-hot platinum sponge, a white deposit was once obtained which resembled sulphuric anhydride, and dissolved in water with a hissing noise, yielding a solution containing selenic as well as selenious acid; but a second experiment made in the same manner yielded nothing but selenious acid (v. Gerichten, *loc. cit.*)

METALLIC SELENATES. On the Optical properties of these Salts, see LIGHT (p. 1190).

Ammonium selenate, $(\text{NH}^4)^2\text{SeO}^4$, when heated, first gives off ammonia, and is converted into the acid selenate, $(\text{NH}^4)\text{HSeO}^4$, and the latter, when further heated, is resolved into selenium, selenious oxide, water, and nitrogen (Cameron a. Davy, *Chem. News*, xxxviii. 133).

Seleniosulphates (v. Gerichten, *loc. cit.*)—Double salts of the form $K^2SeO^4.M'SO^4 + 6H^2O$ [$M = Ni, Co, Fe, Zn, Mn, Cd, Cu, Mg$], are prepared by mixing concentrated solutions of the corresponding sulphates with potassium selenate. They crystallise well, and are isomorphous with the corresponding double sulphates and double selenates. In a similar manner are prepared the corresponding salts $M''SeO^4.K^2SO^4 + 6H^2O$. The *copper salt* crystallises in fine well-formed light blue monoclinic combinations, sometimes tabular, but more frequently prismatic, with great elongation of the basal pinacoid. All these salts are isomorphous with the corresponding double selenates.

Seleniosulphuric Alums.—The salt $K^2SeO^4.Al^2(SO^4)^3 + 24H^2O$ is obtained in limpid octohedrons by mixing the solutions of potassium selenate and aluminium sulphate, and the corresponding chromic, ferric, and manganic alums are obtained in like manner. The salt $K^2SO^4.Al^2(SeO^4)^3 + 24H^2O$ is likewise obtained in transparent octohedrons by mixing the solutions of potassium sulphate and aluminium selenate; so also the corresponding chromic and ferric alums.

Seleniocyanates.—The *potassio-platinic salt*, $K^2Pt(CSeN)^6$, is formed on mixing the alcoholic solutions of potassium seleniocyanate and platinic chloride, and separates from the boiling and filtered liquid in crystals which may be purified from an admixed reddish salt by recrystallisation from alcohol. They are hexagonal plates, generally small, almost black by reflected, dark garnet-red by transmitted light. Sp. gr. = 3.377 at 10° (weighed in benzene). The *gold salt*, $KAu(CSeN)^2$, was obtained in a similar manner in dark red very easily decomposable prisms (J. W. Clarke, *Iber.* xi. 1325).

SELENIUM-BISMUTH-GLANCE, or Frenzelite. This mineral, from Guanajuato in Mexico, crystallises in the orthorhombic system, is isomorphous with antimony-glance, and exhibits the faces $\infty P \infty$, $\infty P \infty$, ∞P , together with several unmeasurable faces, ∞Pn . Sp. gr. 6.25 at 21° . An analysis by Frenzel (*Jahrb. f. Min.* 1874, 679) gave 67.38 per cent. Bi, 24.13 Se, and 6.60 S, agreeing approximately with the formula $2Bi^2Se^3 + Bi^2S^3$, which requires 68.35 Bi, 26.07 Se, and 5.28 S.

SELENIUM-COMPOUNDS, ORGANIC. *Ethyl selenide* or *Selenethyl*, $(C^2H^5)^2Se$, is produced by the action of phosphorus pentaselenide on potassium ethylsulphate. For this purpose, equivalent quantities of these two compounds and potassium hydroxide are digested with a small quantity of water at 50° , and the product is subjected to fractional distillation. The distillate consists for the most part of ethyl monoselenide, contaminated, however, with traces of diselenide, which are removed by digesting the distillate with more potassium ethylsulphate, potash, and water, with addition of a little phosphorus, and distilling afresh.

Pure ethyl monoselenide, thus obtained, is a clear, colourless, mobile, highly refractive liquid, smelling like the light hydrocarbons and boiling at 108° . It mixes with alcohol and ether in all proportions.

Triethyl-selenonium Iodide, $Se(C^2H^5)^3I$.—Ethyl monoselenide and ethyl iodide, when mixed in molecular proportions, combine slowly at ordinary temperatures to form white crystals of this compound. It is stable in the air, not hygroscopic, but very easily soluble in water and alcohol, and sparingly in ether. It sublimes completely between 80° and 126° without melting, and is at the same time resolved into ethyl monoselenide and ethyl iodide, which collect in the receiver and recombine in the course of twelve hours to form triethyl-selenonium iodide.

Triethyl-selenonium Hydroxide, $Se(C^2H^5)^3OH$, is formed by the action of silver oxide on triethyl-selenonium iodide. It is a powerful base, forming a syrupy solution which absorbs carbon dioxide and water with avidity. Its salts are all crystalline: they have the odour of leeks and a burning bitter taste. With the exception of the tartrate, they all deliquesce rapidly in the air, and hence cannot well be analysed.

The *tartrate*, $Se(C^2H^5)^3C^4H^4O^6 + 2H^2O$, crystallises in delicate needles of a pale rose-red colour; it dissolves very easily in water, forming an acid solution.

The *platinochloride*, $[Se(C^2H^5)^3Cl]^2PtCl^4$, crystallises in highly refractive red rhombohedrons.

These results point to the conclusion that selenium is an element of variable atomicity, being bivalent in the compound $(C^2H^5)^2Se$, and quadrivalent in the compounds $(C^2H^5)^3SeC^2H^5I$ and $(C^2H^5)^3SeC^2H^5(OH)$ (L. v. Pieverling, *Liebigs Annalen*, cxxxv. 331).

On *Methyl Selenide* or *Selenmethyl* and its Compounds, see Jackson (p. 1304).

On *Benzyl Selenides*, *Benzyl Seleniocyanate*, *Benzylselenious acid*, and *Benzylselenonium Compounds*, see Jackson (pp. 316, 321).

On *Seleniobenzamide*, $C^6H^5.CSe.NH^2$, see v. Dechend (p. 157).

SEMIPHENOL-CINCHONIDINE, $2C^{20}H^{24}N^2O.C^6H^6O$. See CINCHONA-BASES (p. 487).

SENEGIN. Saponin from Senega-root (p. 1780).

SEPIOLITE. See MEERSCHAUM (p. 1269).

SERANIM. An explosive mixture formed of potassium chlorate and nitroglycerin (Nobel, *Monit. scient.* [3], vi. 248).

SERICITE-ROCKS. See *Jahrb. f. Min.* 1878, 264, 296, 383; *Chem. Soc. J.* xxxvi. 23, 25, 207.

SERPENTINE. The following are recent analyses of this mineral: 1. Noble serpentine from Snarum (*J. R. Müller, Min. Mitth.* 1877, 25). 2 and 3. Light and dark-coloured pebbles of transparent serpentine from the shores of the islands Iona and Tiree, Scotland (*Stanford, Chem. Soc. J.* xxvi. 19). 4-6. From the bed of magnetic iron ore in the Tilley-Foster mine, Putnam County, New York. 4. White, cauliform to fibrous; sometimes in small granules imbedded in the ore or filling small clefts. 5. Green in thin layers, of lighter or darker colour, sometimes cauliform in small clefts (*Breidenbaugh, Sil. Am. J.* [3], vi. 209). 6. Grey-green in radio-fibrous granules. Sp. gr. 2.4. 7. Light-green translucent serpentine from New Jersey, incrustated with a yellowish mass traversed by bands of chrysotil. Sp. gr. = 2.51 (*Berwerth, Min. Mitth.* 1875, 110):

	SiO ^a	Al ^a O ^a	FeO	MnO	MgO	CaO	K ^a O	Na ^a O	H ^a O	
1.	40.82	2.19	6.01	—	36.78	—	—	—	13.48	= 99.28
2.	37.20	—	6.53	4.19	36.73	5.03	—	—	11.42	= 99.96
3.	43.20	—	5.00	0.94	33.60	5.10	—	—	9.60	= 98.44
4.	42.28	0.86	2.57	—	40.20	1.35	trace	0.48	12.52	= 100.35
5.	41.43	—	2.10	—	40.18	0.95	—	—	13.81	= 98.47
6.	39.38	1.56	13.87	trace	32.25	—	0.17	—	11.90	= 99.13
7.	44.25	0.55	0.79	—	41.40	—	—	—	13.76	= 100.75

The serpentines of Upper Alsace have been examined by B. Weigand (*Min. Mitth.* 1875, 183). They may be divided into a northern group (Bluttenberg or Bressoir) and a southern group (Amarinenthal). The northern group includes three kinds of serpentine, all imbedded in gneiss, but showing by the difference of their chemical and microscopical characters that they have originated from different rocks, the serpentine of Bonhomme (No. 1) being derived from olivine-rock, that of Starkenbach from a bronzite rock poor in olivine, that from the Rauenthal (No. 2) from a hornblende rock. In the south, the serpentine (No. 3) is associated with gabbro, consisting —together with felspar, quartz, and diallage—of a fine-fibred hornblende impregnated with quartz, which is sometimes almost wholly predominant, and has probably formed the material for the conversion of the rock into serpentine.

1. Bonhomme; *a* and *b*. Blackish-green serpentine; *c*. Noble serpentine from the clefts.

2. Rauenthal; *a*. Solution obtained by the action of dilute hydrochloric acid continued for several days on the pulverised serpentine; *c*. Total analysis; *d*. Hornblende-rock, probably the matrix of the serpentine, into which it gradually passes.

3. Amarinenthal.

	SiO ^a	MgO	CaO	FeO	Fe ^a O ^a	Al ^a O ^a	Na ^a O	K ^a O	H ^a O	
1 a.	41.13	41.88	trace	2.77	3.86	0.84	trace	trace	10.88	= 101.36
b.	41.1	42.8	—	6.37	—	0.06	—	—	undet.	
c.	39.96	37.41	0.26	6.66	—	0.63	0.72	0.24	16.85	= 102.73
2 a.	37.706	36.602	1.677	10.428	—	0.201	—	—	13.386	= 100
b.	31.098	26.714	5.470	8.847	—	12.701	—	—	15.170	= 100
c.	36.944	36.022	1.393	3.956	6.868	1.353	—	—	13.069	= 99.625
d.	46.407	26.252	10.642	2.107	4.619	6.727	—	—	3.584	= 100.368
3.	39.171	37.033	—	4.000	4.056	1.797	—	—	13.722	= 99.779

In 1a also traces of MnO, NiO, and Cr^aO^a; in 2a and 2b, traces of NiO.

An elaborate memoir on the serpentines of Zöblitz, Greifendorf, and Waldheim in Saxony, containing numerous analyses, has been published by J. Lemberg (*Zeitschr. geol. Ges.* xxvii. 531; *Jahresb. f. Chem.* 1875, 1262). The chemical examination shows that the matrix of the Zöblitz and Greifendorf serpentines consisted of olivine, garnet, and hornblende, the olivine having been converted into serpentine, the garnet

for the most part into chlorite, whilst the hornblende has opposed the greatest resistance to alteration. Veins containing felspar are in many places separated from the serpentine by contact-zones, mostly formed of hornblende. These veins, in the neighbourhood of the serpentine, and sometimes throughout their entire thickness, are converted into masses resembling serpentine and steatite. No undecomposed olivine has yet been found in the serpentine of Waldheim.

On the Serpentine and other rocks in which the Pyropes of Meronitz in Bohemia are imbedded, see Doelter (*Min. Mitth.* 1873, 18; *Jahresb. f. Chem.* 1873, 1217).

On Pseudomorphs of Serpentine from the Magnetic Iron deposit of the Tilley-Foster Mine, see J. D. Dana (*Sill. An. J.* [3], viii. 371, 447; *Jahrb. f. Min.* 1875, 310; *Jahresb. f. Chem.* 1874, 1285-1287).

On Serpentine and Fassaite in forms of Monticellite, see G. vom Rath (*Jahrb. f. Min.* 1875, 413; *Jahresb. f. Chem.* 1874, 1289).

On the Serpentine rock of the Lizard, Cornwall, see King a. Rowney (*Phil. Mag.* [5], i. 280). On the Serpentine and Olivine rock of north Norway: K. Pettersen (*Jahrb. f. Min.* 1876, 613). On Serpentine from the Granulite district of Saxony: E. Dathe (*ibid.* 235, 337).

On the Serpentine of Verrayes (Aosta), see Cossa (*Bull. Soc. Chim.* [2], xxxi. 130; *Chem. Soc. J.* xxxvi. 362).

SERUM ALBUMIN, CASEIN, and GLOBULIN. See PROTEIDS (pp. 1683, 1684).

SESAME OIL. On the detection of this oil, see OILS (p. 1428).

SESQUIPHENOLCINCHONIDINE, $30^{20}H^{20}N^2O.2C^6H^6O$. See CINCHONABASES (p. 486).

SHEA-BUTTER, or GHEA-BUTTER. The fat of *Bassia Parkii*. See v. 238, and further, C. Deite (*Dingl. pol. J.* cccxxi. 168; *Chem. Soc. J.* xxxvi. 568).

SIEGBURGITE (A. v. Lasaulx, *Jahrb. f. Min.* 1875, 128). A fossil-resin occurring in considerable quantity in the lignite-sand and sandstone overlying the beds of lignite in the neighbourhood of Troisdorf and Siegburg, on the northern border of the Siebengebirge. The sand, which consists of fine, white, often limpid quartz-granules, contains small quantities of silver-white mica, and blackish or brownish grains of coaly substance, together with greyish-white, kidney-shaped, or nodular concretions, the particles of which are cemented together by an easily inflammable resin. On breaking the lumps, which are moderately hard and compact, the resin appears in small golden-yellow to brown-red and hyacinth-red granules, for the most part somewhat uniformly distributed between the sand-grains. The proportion between resin and sand varies considerably; in some of the concretions, the resinous cement is so finely distributed as to be scarcely visible, even under a magnifier, although sufficiently abundant to take fire when the lump is held in a flame; in others it is very abundant, sometimes amounting to more than 60 per cent., and appears in the interior of the lump, in easily separable pieces, larger than peas, and having a conchoidal fracture. Its hardness is 2 to 2.5, therefore the same as that of amber, and it cannot be scratched with the nail. After it has burnt away, the lumps fall to pieces.

The resin melts easily, and burns with a yellow, very smoky flame, emitting a pleasant aromatic odour, totally different from the stinking bituminous odour given off by retinite. It is burned for incense in the churches of the district. When distilled it gives off a light, greenish-yellow oil, smelling somewhat like petroleum; this distillate does not deposit succinic acid. The resin is but partly soluble in ether, to which it imparts a faint yellow colour; the ether, when evaporated, leaves a yellow oil, but no crystalline deposit. The resin is likewise only partly soluble in alcohol, and almost insoluble in oil of turpentine.

An analysis of a single specimen gave 85.139 per cent. carbon, 7.904 hydrogen, and 6.957 oxygen; a mixture of the resins from several lumps gave 81.37 per cent. C., 5.26 H., and 13.37 O. The former analysis may be represented by the formula $C^{85}H^{7.9}O^6$; the latter by $C^{81}H^5O^6$. These results show that the composition of the resin is variable, and that the difference of composition in different specimens is due to more or less advanced oxidation.

Only four other fossil resins are known, containing a proportion of carbon approaching to that of Siegburgite, viz.: (a). *Rosthornite*, from the coal beds of the Sonnberg in Carinthia (*Chem. Soc. J.* [2], ix. 1174). (b). *Girona*, or *Bucaramanga resin*. (c). *Copaline*, or *Highgate resin*, from the blue clay of Highgate-hill. (d). *Krantzite*, from the lignite of Lattorf, near Nieburg:

	a	b	c	d
C =	84.42	82.7	85.73	79.25
H =	11.01	10.8	11.50	10.41
O =	4.59	6.5	2.77	10.34

All these resins are distinguished from Sieburgite by their physical properties as well as by their composition. Rosthornite is soft, and may be scratched with the nail; it differs also from Sieburgite in its relations to solvents. Girona resin is more like Sieburgite, but contains less oxygen. Highgate resin contains about the same amount of carbon, but a larger proportion of hydrogen, and much less oxygen; it differs also from Sieburgite in emitting an aromatic odour when broken, whereas Sieburgite does not emit such an odour, even when rubbed. Krantzite is a soft, flexible resin, differing from Sieburgite both in composition and in physical properties.

A variety of retinite is found in the lignite beds of Friesdorf, and another in those of Roisdorf, in the same locality.

SIKERANINE. An alkaloid occurring, according to Buchheim (*N. Rep. Pharm.* xxv. 344), in the mother-liquors of the extract of houbane seeds, from which hyoscyamine has been separated.

SILICA, SiO_2 . On the occurrence and formation of crystallised silica, see QUARTZ (p. 1371).

Hydrate.—Transparent hydrated silica, having the properties of hydropthane, may be obtained by pouring a layer of dilute oxalic acid on a solution of an alkaline silicate in a vessel inclined at an angle of 45° , and leaving the liquid at rest for several months. A layer of transparent silica then forms at the surface of contact of the two liquids, and below this are formed layers of gelatinous silica which gradually fill the vessel.

The hydrated transparent silica thus produced scratches glass, contains much hygrometric water, which it loses at a low temperature (30° – 35°), becoming at the same time milky like opal, and of the same hardness; in this state it also retains 9–13 per cent. of water. Its density varies from 2.03–2.07, and it is singly refractive. Portions which have become opaque by exposure to air or by heating, become translucent when treated with water, thus resembling hydropthane. After exposure to a red heat, this hydrated silica has a mother-of-pearl lustre, is very brittle, exhibits cleavage in its longitudinal direction, and dissolves in a boiling concentrated solution of potash. The gelatinous silica formed at the same time becomes, in the course of a few months, transparent and very hard, and exhibits the properties of hydropthane (E. Monier, *Compt. rend.* lxxxvi. 1318).

Ullik (*Ber.* xi. 2124) finds that the gelatinous silica which separates after some time on pouring a somewhat dilute solution of sodium silicate (water-glass) into hydrochloric acid, may be completely washed by repeated treatment with water, without the slightest loss of coherence. In this manner, perfectly pure silica is obtained as a translucent gelatinous mass of quite unaltered shape, which dries up in the air to a transparent substance resembling hyaline, and splitting up into larger or smaller pieces; it has the density of opal, and approximately the composition $\text{SiO}_2 \cdot \text{H}_2\text{O}$. The lumps, when quickly heated to redness, crumble to a shining sand, but by raising the temperature gradually, larger unbroken pieces may be obtained, perfectly vitreous and transparent, and still to a certain extent hygroscopic. The specific gravity, determined immediately after ignition, is 2.323, which is that of tridymite. The gelatinous silica, obtained as above, possesses in a high degree the properties of a membrane, and being a substance of known composition, should be well adapted for the study of the laws relating to dialysis.

When a solution of a silicate is mixed with an alkaline solution of alumina, a precipitate is formed, consisting of silica or alumina, accordingly as one or the other of these substances is in excess. The dialysis of such a solution has been studied by H. Le Chatelier (*Compt. rend.* lxxviii. 1046). The solution employed contained 0.20 gram SiO_2 , 0.30 Al_2O_3 , and 3.80 Na_2O . On dialysis there remained on the membrane a white pulverulent precipitate containing 0.120 g. SiO_2 and 0.115 alumina; the whole of the alkali had passed through the membrane, and contained in solution 0.105 Al_2O_3 and 0.010 SiO_2 . H. Sainte Claire Deville remarks (*ibid.* 1048) that such a decomposition by dialysis may afford an explanation of certain natural phenomena, in which clay or even chalk may be supposed to play the part of the membrane, and thus the presence of flints in chalk may be accounted for.

Action on Carbonates.—When silica is heated with sodium carbonate in a platinum crucible, the quantity of carbon dioxide evolved tends to a fixed limit, which cannot be exceeded at any particular temperature, but rises steadily with increase of temperature. If y denote the loss of carbon dioxide and x the time, the relation may be expressed by the equation:

$$y = \frac{ax}{b + x}$$

An acid silicate is first formed, and then resolved into a normal silicate and free silica, which again acts on the silicate, and so on till an equilibrium has been established between these opposite actions. The evolution of carbon dioxide is accelerated by passing a stream of dry air into the crucible; but the decomposition is then never complete. Titanic acid acts on carbonates in a similar manner, and so, according to Hiortdahl, does zirconia (v. 1084).

SILICATES. *Behaviour at high temperatures.*—Silicates which do not contain any volatile constituents suffer no chemical change when fused, and some of them even reassume their crystalline form on solidification, but the greater number form a glass which has a lower specific gravity than the original mineral, and is easily decomposed by acids. There is, however, a very important class of silicates, including topaz, mica, tourmaline, &c., which undergo chemical change on fusion, owing to the volatilisation of some of their constituents, as hydrogen and fluorine.

Experiments made with various kinds of topaz and mica show that only the former lose the whole of their fluorine at the temperature of a porcelain-furnace, and that too only under favourable circumstances. One part of the fluorine is evolved as hydrofluoric acid, and the rest as the silicofluoride contained in the original mineral, whilst the metals K, Li, Mg, Fe, Al, and Si, existing as fluorides, remain behind as oxides. This shows that the fluorine in these silicates is combined in a manner similar to the oxygen. In the topazes, not only the silicon of the aluminium silicofluoride, but also a portion of the silicon from the oxy-silicates, is converted by the hydrofluoric acid into silicon fluoride, and evolved as such (Rammelsberg, *Ann. Phys. Chem.* [2], vii. 146).

Analysis.—To estimate the silica in silicates, Maskelyne & Flight (*Ber.* vi. 1414) heat the mineral with *hydrofluoric acid* in a platinum retort through which a stream of hydrogen is passed, and receive the gaseous silicon fluoride thereby evolved in aqueous ammonia of sp. gr. 0.88. The retort is first heated in a water-bath for two hours, whereby the mineral is decomposed, but only a trace of silicon fluoride is evolved, afterwards in a paraffin-bath at 132°, whereupon the silicon fluoride passes over, the operation being completed in five to ten minutes. The process is then repeated with fresh hydrofluoric acid and ammonia-solution to ensure that the decomposition is complete. The ammoniacal solutions are then evaporated in a platinum dish, whereby the silica is dissolved; the cooled solution of ammonium silicofluoride is precipitated with potassium chloride and absolute alcohol; and the silicon is estimated as potassium silicofluoride. One advantage of this method is that the potassium silicofluoride weighs four times as much as the corresponding silica, an important consideration in the case of minerals poor in silica. For the success of the operation, the digestion for two hours in the water-bath is indispensable. Addition of sulphuric acid is to be avoided, as it serves only to retard the distillation of the silicon fluoride.

The decomposition of silicates by hydrofluoric acid is recommended by A. R. Leeds (*Zeitschr. anal. Chem.* 1877, 323), when it is desired to estimate the iron as ferrous oxide. The reaction must be conducted in an apparatus in which the solution is protected from contact with the air.

For the decomposition of silicates and estimation of the alkalis therein contained, A. Terrell (*Compt. rend.* lxxxi. 1268) recommends the use of *barium hydrate*, as it melts easily and at a comparatively low temperature, and nevertheless effects a complete decomposition of the silicate. The finely pulverised substance is fused with 7 or 8 times its weight of fused barium hydrate at the lowest possible temperature (below dull redness) in a silver or platinum crucible, which under these circumstances is not sensibly attacked, especially if the air be excluded; the mass after cooling is boiled several times with water; the excess of baryta and lime, if present, is removed by carbonic acid; and the alkalis are determined in the filtrate by known methods.

G. Bong (*Bull. Soc. Chim.* [2], xxix. 50) effects the decomposition by fusing the finely pounded mineral in a platinum crucible with about three times its weight of pure *red lead*; the fused mass is then digested with nitric acid; the solution evaporated to dryness; the residue treated with water; the solution filtered from the insoluble silica is freed from lead by hydrogen sulphide; and the analysis is completed in the ordinary way. This method also has the advantage of effecting the decomposition at a much lower temperature and in a shorter time than that of fusion with sodium carbonate, and, moreover, greatly facilitates the estimation of the alkalis.

For the estimation of water in silicates, the following method is described by L. Sipöcz (*Wien. Akad. Ber.* [2 Abth.], lxxvi. 51). The silicate mixed with four times its weight of a mixture of potassium and sodium carbonate is placed in a platinum-boat provided with an overlapping cover, which is thrust into the middle of a platinum tube 40 cm. long and 17 mm. internal diameter. This tube is dried by heating it to 130° and passing a stream of dry air through it for about an hour after

which it is laid in a combustion-furnace, and the mixture is thoroughly ignited, while a stream of dry air is continuously passed through the tube. The water which passes over is condensed in an absorption-tube containing fragments of glass moistened with strong sulphuric acid.

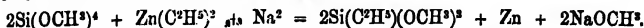
SILICON, or SILICIUM. On the Specific Heat of Silicon, see **HEAT** (pp. 926-927).

On the Estimation of Silicon in Pig-iron, see p. 1108.

Organic Compounds of Silicon:

Ethyl Orthosilicoacetate, $\text{Si}(\text{CH}_3)(\text{OC}^2\text{H}_5)^2$, homologous with ethyl orthosilicopropionate (vii. 1082), is formed, together with zincmethylethoxyl, $\text{Zn}(\text{CH}_3)(\text{OC}^2\text{H}_5)$, by the action of zinc-methyl on ethyl silicate, and may be separated from the product by fractional distillation, as a liquid boiling between 145° and 151° . It resembles the corresponding propionic ether, has a density of 0.9283 at 0° , is soluble in alcohol, insoluble in water, but slowly decomposed thereby. Hydriodic acid converts it into silico-acetic acid, CH_3SiOOH , which is an amorphous powder insoluble in water and in ether, and burns when strongly heated, producing silica, carbon dioxide, and water (Ladenburg, *Ber.* vi. 1029).

Methyl Orthosilicopropionate, $\text{Si}(\text{C}^2\text{H}_5)(\text{OCH}_3)^2$, is obtained by gradually adding sodium (12 grams) to a warmed mixture of methyl silicate (40 g.), and zinc-ethyl (12 g.), then distilling and fractionating the product:



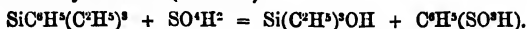
This is a liquid closely resembling the corresponding ethyl ether in odour and appearance, but less stable. Sp. gr. 0.9747 at 0° . Boiling point 125° – 130° . It is insoluble in water, but decomposes in contact therewith, especially on addition of ammonia, yielding silicopropionic acid; readily acted upon also by aqueous hydriodic acid (Ladenburg, *Ber.* v. 1081).

Silicic Phenyltrichloride, or **Silico-benzenyl Trichloride**, $\text{SiC}^6\text{H}_5\text{Cl}_3$, is formed, together with mercuric phenylchloride, by heating mercury-diphenyl with silicon tetrachloride in sealed tubes at 300° . When separated from the product by repeated fractionation, it is a colourless fuming liquid, having a faint odour like that of silicic chloride, and boiling at 197° . It sinks in water and decomposes slowly; quickly, on the other hand, when heated, or on addition of ammonia, yielding silico-benzoic acid, $\text{SiC}^6\text{H}_5(\text{OH})^2$. It is likewise decomposed by absolute alcohol, with formation of ethyl silicobenzoate, $\text{SiC}^6\text{H}_5(\text{OC}^2\text{H}_5)^2$, which is a colourless liquid having an ethereal and at the same time pungent odour (probably due to impurity), boiling at 237° , and having a sp. gr. of 1.0133 at 0° , 1.0055 at 10° . By contact with the air, or more quickly by the action of water, it is converted into a polyorthobenzoic ether. With hydriodic acid it yields, together with ethyl iodide, a hard mass mostly coloured by free iodine, which, after purification by addition of ammonia, repeated evaporation with water, and washing of the residue with water, consists of silico-benzoic acid, the identity of which with that prepared from the chloride has, however, not yet been established. Both these acids dissolve in ether, in aqueous and alcoholic potash, and sparingly in alcohol, but are nearly insoluble in water, and both are converted into silicobenzoic anhydride, $(\text{SiC}^6\text{H}_5\text{O})_2\text{O}$, by precipitating their solution in absolute alcoholic potash with carbon dioxide, filtering, evaporating the filtrate, and drying the residue at 100° . This anhydride dissolves with moderate facility in ether, and remains on evaporation in transparent brittle spherical masses resembling Prince Rupert's drops. It is slightly soluble in alcohol; water takes up only traces of it. It dissolves readily in warm aqueous potash, and is not precipitated from the solution by dilute hydrochloric acid, but on adding ammonia in excess, nearly the whole is precipitated as silicobenzoic acid. When the potash-solution is evaporated to dryness and the residue further heated, water distils over together with benzene. Silicobenzoic anhydride, when heated in contact with the air, is converted into a somewhat fluid, scarcely coloured mass, and this when further heated gives off combustible vapours, and leaves a black tumefied mass which does not burn away completely even at a white heat. Silicobenzoic acid is intermediate in its chemical relations between silicic and benzoic acids (Ladenburg, *Ber.* vi. 379).

Silicic Phenyltriethide, $\text{SiC}^6\text{H}_5(\text{C}^2\text{H}_5)^2$, is produced, together with zinc chloride, by heating about equal quantities of silicic phenyltrichloride and zinc-ethyl in sealed tubes at 150° for some hours, then, after opening the tubes, continuing the heating for an equal time at 180° , and, after a further evolution of gas, at 165° till no more gases are given off on further heating. The contents of the tubes are then to be

cautiously dropped into water, the zinc oxide thereby separated dissolved in hydrochloric acid, and the oily layer, after addition of ether, evaporated, washed, dried, and fractionated.

Silicic phenyltriethide is a colourless liquid boiling at 230° , and giving off a vapour which has an odour like that of oil of cloves but fainter. Sp. gr. = 0.9042 at 0° . It is insoluble in water, but soluble in ether; burns with a bright but very smoky flame. When treated with very strong nitric acid, it turns black and gives off the odour of nitrobenzene. Dilute nitric acid does not act upon it at ordinary temperatures, but decomposes it when heated, likewise with separation of the phenyl-group. Silicic phenyltriethide, heated with strong sulphuric acid, is decomposed, apparently with formation of triethylsilicic acid (vii. 1083):

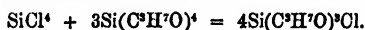


Silicic phenyltriethide, heated with bromine in a reflux apparatus, is converted, with evolution of hydrogen bromide, into a bromo-derivative boiling at 270° – 280° . On slowly passing chlorine into silicic phenyltriethide, the liquid being cooled from time to time, again treating the portion which boils below 250° with chlorine, washing the product with a small quantity of water, and fractionating it after drying with calcium chloride, a small quantity of a thick liquid is obtained, having the composition $\text{SiCl}_2\text{H}^{19}\text{Cl}$. It has an aromatic odour, a density of 1.0185 at 0° , boils at 260° – 265° , burns with a smoky, green-edged flame, is insoluble in water, and is not decomposed thereby; does not yield acetic ether when boiled with alcohol and potassium acetate.

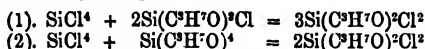
The action of zinc-ethyl on silicic phenyltrichloride yields, in addition to silicic phenyltriethide, two other bodies, one of which appears to be silicic ethide, $\text{Si}(\text{C}^2\text{H}_5)_4$, boiling at 147° – 152° (vii. 1084), the other silicic diphenyldiethide, $\text{Si}(\text{C}^6\text{H}_5)_2(\text{C}^2\text{H}_5)_2$, boiling at about 310° (Ladenburg, *Liebig's Annalen*, clxxiii. 151; *Ber.* vii. 387).

Silicopropyl-compounds (Cahours, *Compt. rend.* lxxvi. 1383). *Silicopropyl ether*, $\text{Si}(\text{C}^3\text{H}_7\text{O})_4$, is formed on adding anhydrous propyl alcohol by small portions to silicic chloride, and is obtained by rectifying the product, as a colourless liquid of sp. gr. 0.915 at 18° , and boiling at 225° – 227° . It is readily decomposed by boiling water, with separation of silica.

Silicopropyl monochloride, $\text{Si}(\text{C}^3\text{H}_7\text{O})_3\text{Cl}$, is formed by heating silicon chloride with silicopropyl ether in closed vessels at 160° :



It has a sp. gr. of 0.980 , and boils at 208° – 210° . *Silicopropyl dichloride*, $\text{Si}(\text{C}^3\text{H}_7\text{O})_2\text{Cl}_2$, is formed by the action of silicon chloride on the monochloride at 160° – 165° , or on silicopropyl ether in the requisite proportion:



The dichloride is a colourless liquid of sp. gr. 1.028 , and boiling between 185° and 188° .

Silicic Tolytrichloride, $\text{SiC}^7\text{H}_7\text{Cl}_3$, is prepared by heating mercury-tolydide (m. p. 238°) with silicon chloride at 300° – 320° , and fractionally distilling the product. It is a strongly refracting, fuming, viscid liquid, smelling like silicon chloride, heavier than water, and decomposed thereby. On dropping it into ammonia, a body separates which is insoluble in water, may be conveniently dissolved out by ether, and remains on evaporation of the ether as an oil which gradually changes to a viscid mass, and finally to a white, translucent, hard, amorphous body, this change taking place more quickly at the heat of the water-bath. This body, after drying at 100° , gave numbers intermediate between those required by the formula of silicotoluic acid, $\text{C}^7\text{H}_7\text{SiOOH}$, and those required by its anhydride, $(\text{SiC}^7\text{H}_7\text{O})_2\text{O}$. Silicotoluic acid melts at about 150° , and is completely converted into the anhydride at 200° (Ladenburg, *Liebig's Annalen*, clxxiii. 165; *Ber.* vii. 389).

SILICO-TUNGSTATES OF CAESIUM AND RUBIDIUM. See RUBIDIUM (p. 1767).

SILK. An analysis of silk-cocoons, by A. Renouard, gave the following results:

	In the entire cocoon	In the inner layer	In the outer layer
Gummy substance . . .	29.30	31.47	27.72
Sericin or Fibroin . . .	70.70	68.33	73.28

The gummy substance was obtained by boiling the cocoon with a strong solution of soap, then washing with boiling acetic acid; the insoluble residue was calculated

as fibroïn. Mulder's analysis of silk is regarded by Renouard as incorrect; he stated that silk contained 19–21 per cent. glutinous substance, and 24–25 per cent. albumin (*Biedermann's Centralblatt, für Agriculturchemie*, 1879, 72).

Air-dried silk contains 9.91 per cent. water (Benard, *Dingl. pol. J.* cccxvi. 216).

According to E. Pfeiffer (*Arch. Pharm.* [3], i. 424), the yellow colouring matter of raw silk consists of chlorophyll more or less altered and deprived of its blue constituent; and from the greenish cocoon, or from greenish raw silk, unaltered chlorophyll may be extracted, separable by ether containing hydrochloric acid into its blue and yellow constituents.

In the manufacture of raw silk, the cocoons are immersed in water, with the object of softening but not of dissolving the natural gum by which the threads are held together. Now raw silk owes its colour, strength, and beautiful appearance to the presence of its soluble constituents; and when soft water is used in winding it, the silk is inferior in strength, colour, and general appearance to that obtained when hard water is employed, because the soluble constituents of the silk are more rapidly dissolved by the soft than by the hard water. Soft water may be improved for spinning purposes by the addition of gypsum, magnesium sulphate, or sodium carbonate (Gabba a. Fextor, *Ber.* xii. 17).

Raw silk boiled with baryta-water yields the same products as fibroïn (Schützenberger a. Bourgeois, p. 785). Champion, by treating silk with concentrated baryta-water, obtained an acid, called *sericic acid*, to which he assigns the formula $C^{30}H^{60}N^2O^{14}$ (vii. 1080).

According to J. Löwe (*Dingl. pol. J.* cccxxii. 274), silk dissolves in an alkaline glycerin-copper solution, and is precipitated therefrom by hydrochloric acid in the form of a white jelly. The copper-solution is prepared by dissolving 16 grams of pure crystallised cupric sulphate in 140–160 g. water, then adding 8–10 g. pure glycerin of sp. gr. 1.24, and dropping in soda-ley till the copper precipitate is redissolved.

The presence of cotton in silk-tissues may be detected by means of chromic acid, which unites with the silk-fibro, and dyes it, whilst the cotton-fibre remains uncoloured (Jacquemin, *Compt. rend.* lxxix. 523).

On the Bleaching and Dyeing of Silk, see *Dingl. pol. J.* cccxiv. 99; *Jahresb. f. Chem.* 1877, 1225.

SILVER. Two specimens of native silver from Allemont in Dauphiné, analysed by A. H. Church (*Jahrb. f. Min.* 1874, 715), were found to contain:

	Ag	Hg	Sb		Sp. gr.
A.	71.69	26.15	12.16	= 110	11.10
B.	73.39	18.34	8.27	= 100	10.05

There is probably some error in analysis A. Nies (*Jahresb. f. Chem.* 1874, 1230) suggests that the percentage of antimony is probably 2.16.

Elaborate investigations on ancient specimens of native silver have been published by E. v. Bibra (*Ueber alte Eisen- und Silberfunde. Archäologisch-chemische Skizze*, Nürnberg und Leipzig, 1873).

M. M. P. Muir (*Chem. News*, xxxv. 6) found in one specimen of arborescent silver from the Thames Gold-field in New Zealand, 97.05 per cent. silver, 0.98 mercury, and 1.98 silica and matrix (= 99.26), together with 0.00005 copper and 0.00109 iron.

An analysis by F. Field (*Chem. News*, xxvii. 175) of native brittle silver from Bolivia, gave 78.12 per cent. Ag, 12.01 AgCl, 9.34 Fe₂O₃, and 0.40 Co.

Extraction and Purification.—The amalgamation of silver ores in Chili is now preceded by treatment with cuprous chloride, which acts on silver sulphide as represented by the equation:



The cuprous chloride is prepared by saturating a solution of cupric sulphate with common salt, and boiling the solution with copper turnings. The crushed ores are first treated with the copper solution alone; mercury is then added (20 to 25 pts. to 1 pt. silver); the mixture is agitated in barrels; and the amalgam is subsequently purified by washing with water, any cupric oxide that may be present being removed by ammonium carbonate. If the ore contains chloride or bromide of silver, a quantity of lead is added equal to 25 per cent. of the amount of silver, whereby chloride of lead is formed, and the loss of mercury by conversion into chloride is avoided (Fonseca, *Dingl. pol. J.* ccviii. 396; also Prime, *Amer. Chemist*, iv. 87; *Jahresb. f. Chem.* 1873, 990; and Krönke, *Dingler*. cccxvi. 401; *Jahresb.* 1877, 1122).

The method of Amalgamation practised in Colorado is described by T. Egleston (*Dingl. pol. J.* cccxvi. 517; *Jahresb.* 1877, 1123).

Extraction with Calcium Thiosulphate.—The following process, practised at the Stewart smelting works, Georgetown, North America, is described by W. Brunton (*Dingl. cexxii. 177*). The ores, after being subjected to a chlorinating process, are introduced into round wooden tubs 1·2 m. high and 2·7 m. in diameter. Each tub holds about 2 tons of ore, and is furnished with an agitator and a closely-fitting cover with two ventilators for the conveyance of steam and sulphurous acid. The tubs are filled with the ore, and the latter treated with Hunt and Douglas's liquid (consisting of sodium chloride and ferrous chloride). The mixture is then agitated, and at the same time sulphurous acid and steam are introduced. The whole of the cupric oxide present in the ore is thus dissolved by the ferrous chloride. The reason for the addition of sulphurous acid is that the ferrous chloride would otherwise be converted into ferric chloride by the oxidising ingredients present in the ore, and the copper would then be precipitated. The cupric chloride in presence of sodium chloride converts the whole of the silver sulphide present in the ore into chloride. After the mixture has been agitated in these tubs for five hours, the solution is allowed to settle, then drawn off, and the tubs are again filled with water, steamed and agitated. After two hours' washing with hot water, the apparatus is again stopped and the clear water drawn off. Calcium thiosulphate is now added from a reservoir placed above the tubs, and after agitation for four hours at 38°, the mixture is left to settle and the clear silver solution drawn off. In the case of ores very rich in precious metals it is advisable to repeat this operation before washing with warm water at 40°. Finally the tubs are emptied.

The solution containing the sodium chloride and ferrous chloride is passed through a filter in order to separate mechanical impurities, and then run into tanks filled with iron filings, where the copper is precipitated and the solution brought back to its former condition. The washings are evaporated to 15° B., and submitted to a similar treatment. The silver solution is placed in large precipitating vessels, treated with calcium sulphide, agitated for a few minutes, and left to deposit. The liquid is then run into the regenerating vessels and treated with sulphurous acid, which converts the whole of the excess of calcium sulphide used into thiosulphate. The washings from the treatment with calcium thiosulphate are worked up in a similar manner. When the precipitate in the precipitating vessels is from 125–150 mm. high, it is washed with hot water, dried, and roasted in a small reverberatory furnace at a low temperature, until all the sulphur has been driven off. Fluxes are added if necessary, and the temperature is raised until the whole mass is in a state of perfect fusion. The slags are then removed, and the pure metal skimmed off and poured into moulds. If the slags contain more than 20 ounces of silver per ton, they are worked up again with the ore.

From the Fahl-ores of Baranna, in Mexico.—The ore, containing zinc-blende, galena, iron and copper pyrites, quartz, silver, and a trace of gold, is crushed and roasted with 5 to 7 per cent. of salt. The copper and zinc are then extracted by treatment with cold water, and the copper is precipitated from the solution by iron. From the insoluble residue the silver with a little lead is extracted by solution of sodium thiosulphate, and the silver precipitated by calcium sulphide. This precipitate when roasted gives a metal of 650–700 thousandths fineness, which is purified by cupellation with lead (*Chem. Centr. 1878, p. 830*).

From Silicious Ores.—Round the great Salt Lake in Utah, enormous deposits of spongy silica are found, which have evidently been deposited from hot springs. These deposits contain lead oxide, cupric oxide, ferric hydrate, ferric oxide, and silver chloride in varying proportions. The quantity of the latter is from 1–10 kilograms per ton, but as an average 2·3–2·5 kilograms. The great amount of silica, seldom less than 90 per cent., makes it impossible to extract the silver by smelting, and it has also been found very difficult to extract the silver chloride by alkaline chlorides or thiosulphates. But the following method gives very good results, not more than 100 grams of silver per ton of ore being lost.

One part of the ore is boiled with 3·5 pts. of salt and 3·5 pts. of strong hydrochloric acid until the mass is disintegrated, then the same quantity of hydrochloric acid is added, and 1 pt. of manganese oxide is gradually introduced. When the evolution of chlorine ceases, the liquid is decanted, the residue washed with water, and the silver is precipitated from the solution by iron. To remove lead and a little copper, it must be refined by cupellation. On working on a large scale, the above proportion will be found sufficient for 2–3 pts. of ore. As manganese oxide, pyrites, salt, and coal are plentiful in Utah, this process can be carried out without difficulty (A. Guyard, *Bull. Soc. Chim.* [2], xxv. 99).

From burnt Cuprous Pyrites.—The residues of cuprous iron pyrites which have been burnt in the sulphuric acid manufacture contain small proportions of copper and

silver, amounting to about 3·6 per cent. of the former, and from 15 to 28 dwts. per ton of the latter. Two methods are employed for the recovery of the silver. The first, known as Claudet's, depends on the almost complete insolubility of silver iodide in cold solutions of metallic and alkaline chlorides. It is conducted by lixiviating the burnt residues after calcination with sodium chloride; the first three washings, which contain nearly all the silver, are, after settling, run into precipitating tanks; a sample from each tank is then assayed for silver; and an amount of potassium iodide, calculated as equivalent to the total silver present, is added in solution to the copper liquors, which are, at the same time, diluted with $\frac{1}{10}$ water, and mixed with milk of lime, the whole being thoroughly stirred. The precipitate, consisting of silver iodide, lead sulphate, calcium sulphate, and oxychloride and subchloride of copper, is allowed to settle. The accumulated precipitate is withdrawn and washed with hydrochloric acid to remove copper salts, and then treated with metallic zinc, whereby zinc iodide is formed, with separation of metallic silver and gold if present. The zinc iodide is then dissolved out, standardised, and used instead of potassium iodide, for operating upon a new quantity of copper liquor. It is essential to the success of the process that only very little or no cuprous chloride should be present in the copper liquors, because it separates out on dilution, and, moreover, interferes with the precipitation of the silver iodide.

The second process consists in blowing through the copper-liquors sulphuretted hydrogen diluted with air. Its first effect is to precipitate a far larger proportion of silver than of copper. The hydrogen sulphide is obtained by acting upon 'tank waste' with hydrochloric acid, in large covered tanks. Before blowing, the copper in the solution is estimated by standard potassium cyanide solution, and the blowing is allowed to proceed until the quantity of copper is diminished by 6 per cent. The precipitate, which still contains a little chloride, is washed and filtered, then calcined at a low temperature, whereby chlorides of copper and silver, and oxide and sulphate of copper are produced. This is then ground to rough powder, lixiviated with water to remove copper sulphate, then with hot solution of sodium chloride, which dissolves the silver chloride. The solution, however, contains also copper and some lead sulphate; it is mixed with milk of lime, well washed, to remove calcium chloride, then digested with dilute sulphuric acid to remove oxide of copper, and again washed. After drying, the precipitate has the composition—

Ag	PbO	CuO	Fe ² O ³	CaO	SO ²	Cl	H ² O	Insol. residue	Total
8·77	28·66	3·75	2·61	13·67	31·73	4·70	4·20	1·40	99·49

The value of the silver recovered is about 2s. 6d. per ton of ore worked, the cost by either plan being about 10d. The quantity of these ores treated annually amounts to about 350,000 tons (T. Gibb, *Chem. News*, xxxi. 165).

On the Separation of Silver from Argentiferous Lead, see LEAD (p. 1166).

On the Recovery of Silver from Cast-iron Crucibles in which that metal or its alloys have been fused, see Javorsky a. Priwoznik (*Dingl. pol. J.* ccxvii. 214; *Chem. Soc. J.* xxix. 453).

For the recovery of Silver from solutions of the Cyanide (photographic baths, &c.), E. v. Bibra (*J. pr. Chem.* [2], xiv. 185) recommends, as most expeditious and least costly, the method of precipitating the silver cyanide with sulphuric acid, igniting the precipitate, and dissolving it in nitric acid. On adding hydrochloric acid to the resulting solution, the whole of the silver is precipitated as pure chloride, which may be most advantageously reduced from its ammoniacal solution by metallic zinc.

Physical Properties.—According to Kirmis (*Pogg. Ann.* clviii. 121), the forms of electrolytically precipitated silver vary with the intensity of the current, the concentration of the solution, and the density of the current at particular points. Thread-like masses of silver, called 'moss-silver,' are produced by heating silver sulphide in a current of steam and hydrogen gas (W. M. Hutchings, *Chem. News*, xxxv. 117, 186).

Pseudomorphs of native silver after Stephanite or Brittle Silver-ore, occur at Příbram in Bohemia (G. vom Rath, *Pogg. Ann.* cxi. 266; V. v. Zepharovich, *Wien. Akad. Ber.* [1 Abth.] lxxix. 33).

The specific gravity of pure silver was found by W. Chandler Roberts (*Proc. Roy. Soc.* xxiii. 494) to be 10·57 in the solid, and 9·4612 in the fluid state; that of an alloy of 718·33 pts. silver and 281·07 copper was found by experiment to be 9·9045; by calculation 9·998. Mean coefficient of cubical expansion through 1050 degrees = 0·00011164; therefore coeff. of linear expansion = 0·0003721.

The melting point of pure silver is given by various authorities at 999° to 1034° (v. 277); according to Becquerel it is 1040°; according to J. Violle (*Compt. rend.* lxxxv. 543) pure silver melts at 954°.

Absorption of Oxygen by Silver.—Dumas (*Ann. Chim. Phys.* [6], xiv. 289) found

that when pure silver prepared in the ordinary way was heated in a porcelain flask, it began to give off pure oxygen at 400° – 500° , the evolution of gas going on for six hours, then ceasing, and not being renewed even when the metal was heated to fusion. The silver when cold formed a finely crystallised metallic mass, having a density of 10.512, which is somewhat higher than that usually given for pure silver. The quantity of oxygen thus evolved from a kilogram of silver amounted to 57 cc. at 0° and 760 mm. or by weight to 82 mg., so that the kilogram of metal employed contained only 999.918 grams of pure silver. In a second experiment in which the influence of the atmosphere on the fused silver was greater, 1 kilo. yielded 155 cc. or 226 mg. oxygen, so that the amount of real silver in the kilogram was only 999.774 grams. In a third experiment, performed in a glass tube, the quantity of oxygen obtained was 174 c.c. = 249 mg., showing that the kilogram of metal contained 999.751 grams of pure silver.

This occlusion of oxygen by silver is of great importance with regard to the use of that metal as the basis of determinations of atomic weights, inasmuch as different values must be obtained according to the quantity of oxygen occluded in the particular sample of silver employed in the experiments. Thus, in the experiments of Marignac a. Stas on the atomic weights of silver and chlorine (i. 905), the introduction of the correction required for the occluded oxygen would give the ratio $\text{Ag} : \text{Cl} = 108 : 35.5$ rather than $108 : 35.45$.

The whole of the oxygen occluded in silver may, as already observed, be drawn off by heating the metal in a vacuum at 600° . If, on the other hand, the temperature be raised to the melting point, and oxygen be brought in contact with the silver, the gas is rapidly absorbed, and partly given up again, with spitting, as the metal solidifies, the remaining portion being however retained. *

Reactions.—On the reaction between silver and nickel in the melted state, see NICKEL (p. 1390).

On the Action of Light on Haloid Silver salts, see LIGHT (p. 1231).

The reduction of silver from its salts by pure hydrogen, observed by Russell¹ and others (vi. 718; vii. 660; viii. 1070), was confirmed in the first instance by the experiments of B. Renault (*Compt. rend.* lxxiv. 984); but subsequent observations by the same chemist (*ibid.* lxxvi. 384) seem to show that the reduction is not effected by pure hydrogen, but only when the gas contains traces of arsenetted or siliciuretted hydrogen. On the whole, however, the balance of evidence appears to be in favour of the reduction of silver salts by pure hydrogen.

Estimation.—Soluble thiocyanates precipitate silver completely from its solutions as thiocyanate, CSNAg , and the precipitate is not acted upon by mineral acids. On adding a solution of potassium or ammonium thiocyanate to an acid solution of a silver salt containing a small quantity of ferric sulphate, the whole of the silver is precipitated, while the excess of the thiocyanate solution gives a blood-red colour with the ferric salt, so that the end of the reaction may be very sharply determined.

As ammonium thiocyanate is very hygroscopic, it is advisable, instead of weighing out a definite quantity of this salt, to titrate a solution of it against a solution which contains 10.8 grams of pure silver dissolved in nitric acid, the liquid being made up to 1000 c.c. 10 c.c. of this solution are put into a beaker, together with 5 c.c. of a solution of ferric sulphate (50 grams to one litre of water), 150–200 c.c. of water are added, and the ammonium thiocyanate solution is then allowed to flow in drop by drop until a pale red tint is obtained. This method is applicable in presence of tolerably large quantities of copper. Chlorine, bromine, or iodine may be estimated by precipitation with an excess of a silver solution containing a known amount of silver, and subsequent titration with thiocyanate solution in order to determine the excess of silver added (J. Volhard, *J. pr. Chem.* [2], ix. 217; more fully, *Liebig's Annalen*, xc. 1–61; *Chem. Soc. J.* xxxiv. 743–5).

On the application of this method to the estimation of Silver and Gold in Cupelled Silver, see Lindemann (*Dingl. pol. J.* ccxxvi. 66; *Chem. Soc. J.* xxxiv. 530).

G. Sire (*Ann. Chim. Phys.* [5], ii. 151) points out that, in taking samples from silver objects for the estimation of the silver, it is necessary first to remove the superficial layer, which is richer in silver than the interior, by boiling with nitric acid, or other manipulations. His experiments show that differences of 3 to 4 per cent. may occur, accordingly as the surface-layer, or the metal remaining after this layer has been scraped off, is taken for analysis.

A modification of the Apparatus used in Gay-Lussac's Method of Silver Assaying is described by Sire (*Ann. Chim. Phys.* [4], xxviii. 108; *Jahresb. f. Chem.* 1873, 946).

Compounds of Silver.

On Alloys of Silver with Copper, see COPPER (p. 561).

On Silver-amalgam, see MERCURY (p. 1270).

Silver arsenide, AgAs , is obtained in the form of a white, brittle, very hard, crystalline metallic button, sp. gr. 8.51, when silver arsenate is gently fused with potassium cyanide. It loses arsenic on heating, forming a new compound having the sp. gr. 9.01; fused under a layer of boric acid at a higher temperature, it is converted into Ag^3As , sp. gr. 9.51 (A. Descamps, *Compt. rend.* lxxxvi. 1022).

Reaction of Silver Arsenite with Ammonia.—The light yellow precipitate of silver arsenite is usually said to be soluble in aqueous ammonia. J. R. Santos (*Chem. News*, xxxviii. 94) has however observed that, if the precipitate formed on mixing solutions of silver nitrate and sodium arsenite be washed several times by decantation, it no longer dissolves (at all events not completely) in aqueous ammonia, but assumes a well-marked crystalline character and a deeper yellow colour. In fact, tribasic silver arsenite, Ag^3AsO_3 , is not by itself soluble in ammonia, but dissolves readily therein in presence of alkaline nitrates. By the continued action of ammonia, it is slowly and imperfectly decomposed, being perhaps converted into a salt of argent-ammonium. A silver arsenite containing in combination or admixture a proportion of arsenic larger than that of the tribasic salt, dissolves at once in ammonia without the presence of alkaline nitrates. The solubility of silver arsenite in acetic acid is governed by the same conditions as its solubility in ammonia.

Chlorides. According to v. Bibra (*Ber.* viii. 741), pure argentous chloride can be obtained by the action of hydrochloric acid on argentous citrate (produced by treating argentic citrate with washed and dried hydrogen at 100°). Argentous chloride is a black powder, the greater part of which dissolves in ammonia, the rest in nitric acid. The residue left by nitric acid is also soluble in ammonia. Potassium cyanide also dissolves the body; sulphuric acid dissolves about 2 per cent. of it; acetic acid and potash do not act upon it. Its analysis leads to the empirical formula Ag^4Cl^3 , but its reactions with nitric acid and ammonia seem to show that it is a mixture, not a definite compound. The blackened chloride produced by the action of light on argentic chloride cannot, according to v. Bibra, be regarded as argentous chloride.

According to Carey-Lea (*Sill. Am. J.* [3], xv. 189), the substance produced by the action of light on silver chloride is of a much more permanent character than that formed in the case of the other silver haloids, inasmuch as nitric acid decomposes the bodies so produced from silver bromide and iodide (with separation of silver, and formation of ordinary silver bromide and iodide), but is without action on the substance formed from silver chloride. After five days' action of strong sunshine on moist silver chloride, exposed in a thin layer and frequently stirred up, about 1, per cent. of the chloride is acted upon. The darkened chloride is not acted on by nitric acid of sp. gr. 1.28 in the cold, so that it does not contain reduced silver; but as it is quickly whitened by *aqua regia*, it is probable that the darkening is due to the formation of a subchloride or oxychloride. By digesting the darkened chloride (precipitated in presence of hydrochloric acid) with nitric acid of sp. gr. 1.28, for 18 hours on the sand-bath, a perceptible amount of silver was dissolved.

Darkened silver bromide is readily acted on by the same nitric acid, complete decomposition taking place after heating for some hours.

Silver Chloroplatinite, $\text{AgCl}_2\text{PtCl}_2$, produced by the action of silver nitrate on a solution of potassium chloroplatinite, is an amorphous flesh-coloured precipitate insoluble in water, decomposed by hydrochloric acid (Nilson, *J. pr. Chem.* [2], xv. 269).

On *Silver Ferrocyanide*, see CYANIDES (p. 612).

Effects of Heat on Chloride, Bromide, and Iodide of Silver. G. F. Rodwell* (*Proc. Roy. Soc.* xxv. 280) has described various experiments made for the purpose of determining the coefficients of expansion and contraction of the iodide of silver, and the coefficients of expansion of the chloride and bromide. The results are given in the following table. It will be seen that the coefficients of the chloride and bromide are a little higher than those of the most expansible metals (lead and zinc), and that the coefficient of the bromide is higher than that of the iodide. The iodide of silver, on the other hand, has long been known to exhibit certain anomalies, contracting through a given range of temperature on heating. The following facts have been established in regard to these anomalies. If a mass of the molten iodide be allowed to cool, the following effects may be observed: (α). At the moment of solidification a considerable contraction takes place. (β). The solid on further cooling undergoes slight and regular contraction after the manner of solids in general,

* Communicated by the author.

until it reaches a temperature of 142° , when it undergoes sudden and violent expansion, passing from the amorphous to the crystalline condition. (γ). After undergoing this expansion, the mass, on further cooling, undergoes slight expansion. According to Fizeau, the point of maximum volume is at -60° and the coefficient of contraction augments with the temperature. The iodide exists in two allotropic conditions. Above 142° it is a yellow flexible transparent solid, while at 142° it changes to a pale-green, crystalline, opaque, brittle substance.

EFFECTS OF HEAT ON THE CHLORIDE, BROMIDE, AND IODIDE OF SILVER.

	Chloride	Bromide	Iodide
Fusing point	451°	427°	527°
Specific gravity at 0° . . .	5.505	6.245	5.675
" " fusing point.	4.919	5.595	5.522
Volume at -60°	1.000000	1.000000	1.017394
" 10°	—	—	maximum volume
" 0°	1.005547	1.006060	1.017342
" 70°	—	—	—
" 100°	1.015092	1.016560	1.017009
" 142°	—	—	—
" 200°	1.024937	1.027460	1.015750
" 300°	1.035082	1.038760	after sudden expansion
" 400°	1.045227	1.050460	1.000000
" fusing point (solid).	1.050319	1.053470	maximum density
" " (liquid)	1.116427	1.122840	—
Physical structure, &c. of fused mass.	Crystalline fracture; thin films, transparent and flexible in the cold; thick rods, very flexible while hot.	Crystalline and brittle.	Transparent and flexible above 142° ; crystalline, opaque, and brittle below that temperature.

Chlorobromiodides. Rodwell (*Proc. Roy. Soc.* xxv. 292) has also determined the coefficients of expansion, and other properties, of five compounds of silver with chlorine, bromine, and iodine. Chlorobromides of silver have been found in the mines of Chañarcillo in Chili, also, according to Dana, an iodobromide. The compounds described were formed by fusing together in a porcelain crucible the chloride, iodide, and bromide of silver in such proportions as furnished bodies of the composition shown in the annexed table. The coefficients of expansion having been determined by a method described by Rodwell, the volumes given in the table were calculated therefrom. The melting points were determined by Carnelley, by his new method (p. 937). The following facts will be observed by reference to the table:

1. The chlorobromiodides contract on being heated from 124° – 133° . Hence they possess two points of similar density.

2. While the iodide of silver commences its contraction when the temperature rises to 142° , and ends it at 145.5° , the chlorobromiodides begin to contract 18° lower, and cease to contract at 12° lower.

3. The specific gravity is in all cases above the mean of that of the constituents.

4. The melting points are in all cases lower than those of the constituents. Thus No. 3 melts at 326° , viz. 201° lower than iodide of silver, which constitutes 58 per cent. of its weight.

5. The melting points diminish from No. 1 to No. 3, and increase again from No. 3 to No. 5.

6. The contraction undergone by some of the chlorobromiodides is greater than that of the iodide of silver itself, although it is associated with two such expansible bodies as the chloride and bromide of silver; while, on the other hand, No. 1 has, during certain ranges of temperature, a higher coefficient than any of the substances composing it.

7. These anomalies are, no doubt, due to the way in which the iodide changes from

PROPERTIES OF THE CHLOROBROMIODIDES OF SILVER.

	I AgI, Ag ⁺ Br ⁻ , Ag ⁺ Cl ⁻	II AgI, AgBr, AgCl	III Ag ⁺ I ⁻ , Ag ⁺ Br ⁻ , Ag ⁺ Cl ⁻	IV Ag ⁺ I ⁻ , Ag ⁺ Br ⁻ , Ag ⁺ Cl ⁻	V Ag ⁺ I ⁻ , Ag ⁺ Br ⁻ , Ag ⁺ Cl ⁻
Melting point	383° C.	331° C.	326° C.	354° C.	380° C.
Specific gravity at 0° C.	6.152	6.1197	6.503	5.9717	5.907
Specific gravity calculated on the assumption that no change of volume occurs	5.836	5.801	5.762	5.741	5.725
Specific gravity at melting point	5.5118	5.5673	5.6971	5.643	5.680
Volume at 0° C.	1.000000	1.000000	1.000000	1.000000	1.000000
" " 124° C.	*1.015331	1.012037	1.010301	1.007440	1.006696
" " 133° C.	*1.015037	1.006637	.993201	.984041	.979696
Volume of solid at melting point	1.054986	1.046646	1.032283	1.009612	1.006372
" " liquid at solidification point	1.112376	1.097486	1.059998	1.057645	1.040513
Physical properties of the chlorobromiodides	Yellow, turning green on exposure to light. Crystalline fracture. Brittle. Resembled bromide of silver.	Orange, turning bright green on exposure to light. Semi-crystalline fracture. Tenacious when cold. Bends very slightly before breaking at 250° C.	Orange, becoming green on exposure to light. Very tenacious when cold. Compact; hard. At 250° C. could be bent through an angle of 40° without breaking.	Dull orange, becoming green on exposure to light. Crystalline. Brittle when cold, more flexible at 250° C. than No. 3. Less hard and tenacious when cold.	Orange-yellow, becoming green on exposure to light. Crystalline and very brittle when cold. At 250° C. very plastic. Could be bent easily and twisted. Resembled iodide of silver.
Com- posi- tion in 100 parts.	Iodide of silver Bromide of silver Chloride of silver	26.1692 41.8708 31.9600	58.6404 23.4557 17.9039	68.0174 18.1379 13.8450	73.9285 14.7556 11.2859

* In the case of No. I. these temperatures were respectively 125.5° C. and 131.5° C.

the crystalline to the amorphous condition within the surrounding mass of chloride and bromide. Let us, for instance, consider one case, No. 3, the composition of which is $\text{Ag}^2\text{I}, \text{AgBr}, \text{AgCl}$. 'In every 100 mols. between the temperature of 124° and 133° we have 58 mols. undergoing somewhat rapid contraction, while 42 are undergoing expansion. At the same time, other events are taking place within the mass; heat is disappearing as internal work, and is changing the crystalline into the amorphous iodide; that is, converting an opaque, brittle, highly crystalline body (the iodide alone is here spoken of, not the chlorobromiodide) into a transparent, plastic, denser body. What the precise function of the molecular motion which disappears can be, it is difficult to assume, since in this case it not only changes the state of the body, but likewise approximates its molecules.'

Peroxide. When electrolytically prepared silver peroxide is brought in contact with aqueous ammonia, a violent evolution of nitrogen takes place, and Berthollet's fulminating silver (v. 300) is formed, but remains dissolved in the excess of ammonia. On evaporating a small quantity of this solution in an iron spoon, a dangerous explosion takes place. When the dry and finely pulverised peroxide is moistened with a few drops of oil of cloves, the oil takes fire, and silver having the metallic lustre is separated (Böttger, *Ber.* vi. 1396).

Silver Silicofluoride, Ag^2SiF_6 , is formed on bringing silver nitrate in contact with silicofluoric acid, as a greyish-white precipitate, which is decomposed even by a weak solution of ammonia (S. Kern, *Chem. News*, xxxiii. 35).

SILVER-ULTRAMARINE. See **ULTRAMARINE**.

SINISTRIN, $\text{C}^6\text{H}^{10}\text{O}^5$. This name is given by f. Schmiedeberg (*Ber.* xii. 704) to a carbohydrate occurring abundantly in the squill (*Urginea Scilla*). In external appearance it closely resembles achroo-dextrin, but it is lævogyrate, and is almost wholly converted into lævulose by the action of warm dilute acids. It may be obtained by adding lead acetate to powdered squill made into a thin paste with water, as long as a precipitate is formed, mixing the filtrate, after removal of lead, with excess of calcium hydrate, which precipitates the sinistrin, and decomposing the precipitate with carbonic anhydride, any lime remaining in the liquid being removed by careful addition of oxalic acid. The filtrate is then decolorised by animal charcoal, gently evaporated at 40° – 50° , and the sinistrin precipitated by alcohol. Pure sinistrin, $\text{C}^6\text{H}^{10}\text{O}^5$, is colourless and amorphous: it dissolves in water in all proportions, and in presence of an alkali holds copper oxide in solution without reducing it. Its specific rotatory power is $[\alpha]_D = -41.4^\circ$. Saliva and diastase have no action on sinistrin, but warm dilute sulphuric acid completely converts it into sugar, consisting of a mixture of lævulose with an optically inert variety, both of which are capable of fermentation, and reduce copper oxide in alkaline solution.

The name *sinistrin* is also applied by G. Kühneman (*Ber.* viii. 387) to a lævogyrate substance resembling dextrin, contained in ungerminated barley.

SIPYLITE. A niobate, occurring in Amherst County, Virginia, associated with albanite and magnetite, and occasionally with a few large crystals of hydrous zircon. It appears in small irregularly shaped masses, very brittle, exhibiting small, but distinct conchoidal, and also uneven fracture. Colour, brownish-black, in thin splinters red-brown; streak, light cinnamon-brown; lustre, resinous and pseudo-metallic; translucent in thin splinters; hardness = 6, nearly; sp. gr. 4.89. When heated before the blowpipe the mineral decrepitates and glows brilliantly, becoming pale greenish-yellow and opaque. Its analysis gave:

Nb ² O ⁵ ,Ta ² O ⁵ (*)		WO ³	SnO ²	ZrO ²	Eb ² O ³ ,Y ² O ³ (*)		Ce ² O ³
48.66		0.16	0.08	2.09	27.94		1.37
La ² O ³	Di ² O ³	WO	MnO	FeO	BeO	MgO	
3.92	4.06	3.47	trace	2.04	0.62	0.05	
CaO	Li ² O	Na ² O	K ² O	F	H ² O		
2.61	trace	0.16	0.66	trace	3.19	= 100.48	

(*) Ta^2O^5 = about 2 per cent.

(*) Y^2O^3 = about 1 per cent.

Grouping together the acid oxides of Nb, Ta, W, Sn, and Zr, reducing all the basic oxides present to the equivalent amounts of dyad oxides, and leaving out the water, these numbers may be represented by the formula $\text{R}^2\text{M}^2\text{O}^8.4\text{R}^2\text{M}^2\text{O}^7$ (J. W. Mallet, *Sill. Am. J.* [3], xv. 397).

SIMUM. The root of *Sium latifolium* contains sugar, gum, albumin, pectin, a colourless fragrant volatile oil, and a resin, which appears to be the poisonous constituent (A. R. Porter, *Pharm. J. Trans.* [3], vii. 174). N. Rogers (*ibid.* 433) found

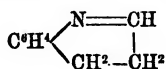
in the root two acid resins and an indifferent resin, from which a body was obtained which crystallised in colourless needles and volatilised without decomposition; also volatile oil, starch, sugar, gum, albumin, salts of potassium, sodium, calcium, and magnesium, and lastly a volatile alkaloïd which he regards as *pastinacine*.

SKATOLE, C^6H^5N (Brieger, *Ber.* x. 1027; xii. 1985; Nencki, *ibid.* x. 1032).^{••} A crystallisable substance, closely resembling indole, found, together with acetic, butyric, and isobutyric acids, and small quantities of phenol and indole, in human excrements (*σκατος*). It is also a product of the fermentation of albuminoids, and is best prepared by the fermentation of blood-albumin with a little pancreas and water, indole being formed at the same time. Skatole crystallises in irregularly dentate, shining plates, resembling indole, which, by frequent recrystallisation from hot water, can be obtained snow-white. The crystals, which have a highly disagreeable faecal odour, melt at 94° – 95° . Skatole is rather less soluble in water than indole, and can be easily distinguished from the latter by not being coloured by chlorine-water, and by the fact that an aqueous solution of skatole, treated with a drop of fuming nitric acid, gives not a red precipitate, but a white cloudiness. It is soluble in warm dilute nitric acid, but separates unchanged on cooling. It is decomposed when boiled for some time with nitric acid, giving off vapours which have the odour of nitro-phenol.

Skatole forms the chief constituent of the volatile aromatic portion of human faeces. The faeces of dogs (whether fed on bread or on meat diet) contain no skatole, but only indole and a volatile yellow oil (not yet analysed), having a revolting and peculiarly irritating odour. The same oil is obtained by distillation from various pathological fluids of the human organism.

Skatole, when administered in small doses, appears to exert no deleterious action on the animal organism, but in larger quantities it produces tetanus, and gives rise to an increase of the proportion of ethylsulphates to sulphates in the urine.

Nencki (*J. pr. Chem.* [2], xx. 466) regards skatole as methyl-indole, $C^6H^4(CH^3)N$, and Ossikovsky (*Ber.* xiii. 332) represents it by the constitutional formula:



An isomeride of skatole, $C^6H^4 \begin{array}{c} \diagup CH^2 \\ \diagdown N \end{array} \gg C(CH^3)$, called *Methyl-ketole*, and regarded as the methyl-derivative of an hypothetical body, *ketole*, $C^6H^4 \begin{array}{c} \diagup CH^2 \\ \diagdown N \end{array} \gg CH$, is formed by treating orthonitrophenyl-acetone, $C^6H^4 \begin{array}{c} \diagup CH^2.CO.CH^3 \\ \diagdown NO^2 \end{array}$, with ammonia and zinc-dust at a temperature just below the boiling point of the mixture. The nitro-compound is then converted into the corresponding amido-compound, $C^6H^4(NH^2).CH^2.CO.CH^3$, and the latter, by loss of H^2O , into methyl-ketole. On distilling the product in a current of steam, the methyl-ketole crystallises from the distillate in colourless plates or needles having a strong odour like that of indole. It melts at 59° , and distils without decomposition at a higher temperature. It dissolves in hot water and in hydrochloric acid, and the acid solution yields with platinic chloride a crystalline double salt, and with picric acid a deposit of yellowish-red needles. With nitrous acid it gives a yellowish, and with bleaching powder a fugitive blue coloration (A. Baeyer a. O. R. Jackson, *Ber.* xiii. 137).

SLATE. Analyses of twenty varieties of Thuringian slates from the neighbourhood of Lehesten, near Gräfenenthal, have been published by H. Mäder (*Arch. Pharm.* [3], iii. 197, 289; *Jahresb. f. Chem.* 1873, 1224). These slates contain no magnesia. The following analyses of 'green slate' from Reichenau in Lower Austria, traversed by veins of epidote and calcspar, are given by Zellner a. Breck (*Min. Mitth.* 1873, 130):

SiO^2	Al^2O^2	Fe^2O^2	FeO	MgO	CaO	Na^2O	K^2O	H^2O	CO^2	
63.69	19.96	10.60	3.52	3.83	5.18	2.20	0.22	2.11	0.70	= 102.01
45.59	12.22	12.30	3.73	2.82	13.02	3.46	trace	1.48	6.05	= 100.67

Analyses by Briegel of slates and slate-clays occurring between Salzbach and Ottenau in the Black Forest have been published by P. Platz (*Jahresb. f. Chem.* 1873, 1226).

1. Soft brown-red micaceous slate, used for sprinkling on the soil of vineyards
2 and 3. Spherical concretions of green and brown slate-clays. 2. Nucleus. 3. Crust.

	SiO ²	Al ² O ³	Fe ² O ³	P ² O ⁵	CaO	MgO	K ² O	Na ² O	Loss by ignition	
1.	51.09	20.94	11.86	0.19	2.07	1.44	7.41	1.05	4.39	= 100.44
					CaCO ³	MgCO ³				
2.	31.11	14.26	4.76	0.39	39.24	8.12	1.83	0.36	—	= 100.07
3.	12.50	7.70	4.20	0.17	51.10	22.61	0.35	1.41	—	= 100.04

The following analysis of a red slaty clay from the Schweighof near St. Märgen in the Black Forest of Baden is given by Vogelgesang (*Jahresb. f. Chem.* 1873, 1226):

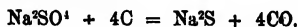
SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	K ² O	H ² O
58.31	25.45	5.44	0.52	1.53	2.31	6.29 = 99.85

SMILACIN, syn. with *Parillin*, the Saponin of Sarsaparilla. See **SAPONIN** (p. 1780).

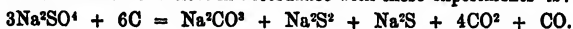
SODA. Elaborate reports on the progress of the soda-manufacture by Le Blanc's process have been published by G. Lunge (*Dingl. pol. J.* cccxiv. 195, 318; *Jahresb. f. Chem.* 1877, 1145; further, *Dingl.* cccxxi. 266, 377, 443; *Chem. Soc. J.* xxxvi. 677, 751).

Experiments by J. Mactear (*Chem. Soc. J.* xxxiii. 475) on the decomposition of sodium sulphate by carbon in various proportions and at different temperatures have led to the following results:

1. When sodium sulphate is mixed with a quantity of carbon in excess of two equivalents, and exposed to a temperature considerably above red heat out of contact with air, the sulphate is ultimately converted into monosulphide of sodium, while the oxygen is evolved as carbon monoxide:



2. When sodium sulphate and carbon, finely divided and intimately mixed, are exposed to a temperature of dull redness (say from 1150°–1300° F.), out of contact with the air, a certain quantity of sodium carbonate is formed, together with an equivalent proportion of sodium bisulphide, as well as monosulphide, while the carbon combines with the oxygen of the sodium sulphate to form carbon monoxide and carbon dioxide. The amounts of carbonate and bisulphide formed vary inversely as the temperature, while the amount of sulphate decomposed varies directly as the temperature. The reaction which is most in accordance with these experiments is:



Any excess of carbon acts apparently in the first instance on the CO₂, reducing it to CO, and finally on the Na₂CO₃ + Na₂S₂, producing Na₂S + CO.

The decomposition of potassium sulphate by carbon takes place at lower temperature, but the decomposition is of the same character as in the case of sodium sulphate, the products consisting of carbonate and bisulphide of potassium.

The following process for the manufacture of carbonate and other salts of sodium is described by Weldon (*Chem. Centr.* 1878, 109). Sodium sulphate is melted in a Siemens' regeneration furnace, and poured on to the requisite amount of red-hot coal contained in a revolving furnace, the inside of which is protected from the action of the molten sodium sulphide by a thick layer of compressed magnesia, coke, or graphite. The carbon dioxide set free during the process is collected in gasometers, and used in the manufacture of sodium bicarbonate. The sodium sulphide is converted into caustic soda by the action of superheated steam. Silicate and phosphate of soda are made by heating a mixture of the sulphide with silica, or with aluminium phosphate, in a current of superheated steam.

Sodium bicarbonate separates out when carbonic acid is passed into a cold solution containing 12.20 per cent. of sodium sulphide. The monocarbonate is obtained by calcining the bicarbonate.

On the recovery of Sulphur from Soda-waste, see Kraushaer (*Dingl. pol. J.* cccxvi. 412; *Jahresb. f. Chem.* 1877, 1148; *Chem. Soc. J.* xxxiv. 171).

On the action of Manganous Chloride at high temperatures on Soda-waste, see Watson Smith (*Chem. News*, xxxvi. 113).

F. Fischer (*Ber.* ix. 1558) has examined the gases given off from the furnaces in Leblanc's soda-process, and finds them to contain, on the average, 16 per cent. carbon dioxide, 6–10 oxygen, and 77–79 nitrogen, but no carbon monoxide. The temperature of the melted mass, taken with a Siemens' pyrometer, was found to vary from 713°–792°.

Ammonia-soda Process. This process consists in decomposing a solution of sodium chloride with ammonium bicarbonate, whereby sodium carbonate and ammonium chloride are produced. The sodium bicarbonate is obtained as a precipitate which is dried and converted by heat into monocarbonate, and the ammonium chloride is heated with caustic lime, the ammonia thereby set free being mixed with the carbon

dioxide produced by heating the sodium bicarbonate, and thereby reconverted into ammonium bicarbonate, to be used for the decomposition of fresh quantities of sodium chloride. The advantages of this process are: the direct transformation of sodium chloride into carbonate; the non-precipitation of other metals from the mother-liquors; the absolute freedom of the product from sulphur-compounds; the simplicity of the plant; the small amount of fuel and labour required; and the absence of noxious gases (R. Wagner, *Dingl. pol. J.* ccix. 282). Nevertheless, the process, when tried on the manufacturing scale, presented so many difficulties, that its prospect of success appeared but small till certain valuable improvements were introduced by E. Solway. The chief difficulties consisted in the loss of ammonia in consequence of imperfect absorption, and the production of large quantities of useless calcium chloride in the decomposition of the ammonium chloride by lime. The loss of ammonia has been prevented to a great extent by passing the mixture of carbon dioxide and ammonia-gas through a vertical cylinder from 35–60 ft. high, provided with a number of false bottoms, through which the solution of sodium chloride trickles downwards, and is thus brought well in contact with the upward-moving gases. The sodium bicarbonate separates in the form of a powder which remains on the false bottoms, and is from time to time collected, dried, and converted into monocarbonate as above mentioned. To avoid the production of calcium chloride, for which there is scarcely any use, the decomposition of the ammonium chloride is effected with magnesia, the resulting solution of magnesium chloride being evaporated, and the residue ignited, whereby hydrochloric acid is evolved, which may be condensed in towers, and magnesia is obtained, which may be used again in the process (Weldon, *Ber.* viii. 782).

Another difficulty experienced in the process arises from a reverse action, by which, under certain circumstances, sodium bicarbonate and ammonium chloride reproduce ammonium bicarbonate and sodium chloride. This, however, may be obviated by due attention to the temperature and concentration of the solutions. According to Günsberg (*Ber.* vii. 644), the proportions of common salt, ammonia, and water should be so regulated that, after the precipitation of the sodium bicarbonate, there should remain a saturated solution of ammonium chloride, containing only a very small quantity of sodium bicarbonate. 100 pts. of a solution of sal-ammoniac saturated at 17° (25·89 p. c.) can dissolve, at ordinary pressure and temperature, 5·742 pts. sodium bicarbonate. According to Honigmann (*Dingl. pol. J.* ccxii. 507), when carbon dioxide is passed into a saturated solution of equivalent quantities of common salt and ammonium carbonate, a mixture of 94 per cent. sodium bicarbonate and 6 per cent. ammonium bicarbonate is precipitated, whilst the liquid contains 12 per cent. sodium chloride and 4 per cent. ammonium bicarbonate, together with 20 per cent. sal-ammoniac. The smaller the quantity of common salt in solution, the greater is the quantity of ammonium bicarbonate precipitated. For these reasons Honigmann suggests the use of an excess of common salt, viz. 1·5 mol. NaCl to 1 mol. ammonium carbonate.

On the Utilisation of Gas-liquors in the Ammonia-soda process, see Gerlach (*Dingl. pol. J.* ccxxiii. 82; *Chem. Soc. J.* xxxii. 236).

The following direct methods of preparing sodium carbonate from the chloride have also been proposed.

C. Bohlig (*Dingl. pol. J.* ccxxiv. 621) heats magnesium oxalate with equivalent quantities of hydrochloric acid and common salt, whereby acid sodium oxalate is precipitated and magnesium chloride dissolved. The acid sodium oxalate, after washing with water, is mixed by agitation in an air-tight barrel with an equivalent quantity of magnesium carbonate and water, whereupon, after the pressure has risen for a time to 2 atmospheres, a concentrated solution of sodium bicarbonate is produced, together with a precipitate of magnesium oxalate. On separating this precipitate and boiling the solution of sodium bicarbonate with magnesia (obtained from the solution of magnesium chloride above mentioned), sodium monocarbonate is produced, together with magnesium carbonate, which may be used over again. The acid solution of magnesium chloride obtained by the first process is evaporated down, the residue heated to redness in a reverberatory furnace, the magnesia thereby produced is employed in the second process, and the undecomposed magnesium chloride is extracted with water, and converted into carbonate by means of the fire-gases from a coke furnace. The oxalic acid required for the process is obtained by the action of boiling potash-ley of 36° B. on deal shavings.

A similar process may be employed for the preparation of potassium carbonate from potassium chloride.

Grüneberg u. Foster (*Dingl. pol. J.* ccxxi. 93) suggest the preparation of sodium carbonate from common salt by means of *alumina*. The salt is mixed with alumina and water to a pulp, and the mass is dried, broken into small pieces, and subjected to the action of overheated steam. Hydrochloric acid then escapes, and sodium aluminate

remains, which may be purified by lixiviation, and decomposed either with carbonic acid for the preparation of sodium carbonate, or with lime for the preparation of caustic soda. The alumina may be replaced by ferric oxide or other metallic oxides. The process is said to be applicable also to the preparation of potassium carbonate and hydrate from potassium chloride.

On the preparation of sodium carbonate from the *nitrate* (Chili saltpetre), see Siebel (*Ber.* vii. 1786; *Chem. Soc. J.* xxviii. 670), and Lieber (*Ber.* viii. 49; *Chem. Soc. J.* xxviii. 671).

SODALITE. An analysis by Fleischer of this mineral from the sodalite-syenite (ditroite) of the Ditro range, is published by G. vom Rath (*Jahrb. f. Min.* 1876, 774):

Cl	SiO ^a	Al ^a O ^a	CaO	K ^a O	Na ^a O	Na	H ^a O
6.08	38.66	32.81	0.95	1.04	13.28	3.93	2.36 = 99.11

SODIUM. *Occurrence in Plants.*—An examination by Contejean (*Compt. rend.* lxxxvi. 1151) of about 600 species of plants by means of the gas blowpipe, has led to the following conclusions. More than three-fourths of terrestrial (non-maritime) plants contain sodium. The sodium is contained in largest quantity in the underground parts of the plants, and the quantity decreases in the higher parts, so that the flowers, the upper part of the stem, and upper leaves contain little or none, whilst the base of the stem, the lower leaves, and the root contain a notable quantity. Aquatic plants contain sodium in all their submerged parts in nearly equal proportion, whilst the parts above the surface of the water follow the same law as in land plants. Plants growing in wet places and in marshes; &c., are richer in sodium than plants growing on dry land, especially in their subterranean parts.

From experiments by Déhérain (*Chem. Centr.* 1878, 783), it appears that beans grown in water containing sodium chloride alone in solution assimilate the salt in small quantities, but that if other salts are present in the water, sodium chloride is taken up only when its proportion is large compared with that of the other salts. The other salts employed were calcium and potassium nitrates. Beans grown in water containing 1 gram of each of the three salts showed no trace of sodium in their ashes; if, however, the proportion of sodium chloride was raised to 4 grams, a small quantity was assimilated. In such a solution the plants lived several days, whereas in one which contained 4 grams of sodium chloride only, the assimilation of that salt was rapid, but the plants very soon died. Soda is taken up from the ground by beans, only when its proportion to the other salts is large, and hence the absence of soda in the ash of the plant does not necessarily prove that the soil in which it was grown was free from soda, but may arise from the soda being mixed with sufficient quantities of other salts.

The laws of diffusion offer no explanation of the fact that sodium chloride is more readily assimilated in the absence of other salts. When beans which had begun to germinate were placed in salt water, they frequently removed more salt than water; Böhm had shown that distilled water cannot support their growth, but that water containing calcium salts readily does so: hence it may be inferred that the germinating beans assimilate by preference calcium and potassium salts, and take up sodium chloride only when the calcium and potassium salts are absent, or are deficient in quantity relatively to the sodium chloride.

All the above facts support the opinion that soda is useless, if not hurtful to most plants. The roots of land plants and the submerged parts of aquatic plants absorb soda without selection, and it is but partially transferred to the upper parts. The proportion of soda in all aquatic plants is also found to be practically the same. In maritime plants, even though soda is present in large quantity in most parts, the flower is never found to contain the smallest trace of this substance.

Preservation of Sodium with bright Metallic Surface.—For this purpose, R. Böttger (*Ber.* vii. 1536) places the metal in a basin containing alcohol till it acquires a perfectly bright surface, then quickly transfers it to a second basin containing chemically pure petroleum-ether, and finally to a third containing a saturated solution of chemically pure naphthalene in petroleum-ether. In this last solution the sodium remains unaltered.

Chloride. This compound separates on cooling from solution in hot hydrochloric acid in needle-shaped hydrated crystals, which contain 94.5 per cent. NaCl, and 5.48 H^aO, and appear to change after some time into the ordinary crystals of the anhydrous salt (*E. Bevan, Chem. News*, xxxv. 17).

According to S. Cabot (*Amer. Chemist*, v. 443), heated sodium chloride is decomposed by the action of air and water-vapour, as shown by the equation $\text{H}^a\text{O} + 2\text{NaCl} = 2\text{HCl} + \text{Na}^a\text{O}$.

E. Chevreul (*Compt. rend.* lxxxv. 493) finds that a solution of the chlorides of

sodium and ammonium containing not more than 1 mol. NH_4Cl to 1 mol. NaCl , yields on evaporation crystals of a double chloride, but that a mixed solution containing any larger proportion of ammonium chloride yields crystals of the latter only. A solution of the chlorides of potassium and ammonium, on the other hand, yields crystals of a double salt, whichever of the two salts may be in excess.

Peroxide, Na_2O_2 . This compound is easily obtained by adding to a solution of sodium hydroxide of about 20 per cent. a solution of 5 per cent. hydrogen dioxide, and then a moderate excess of 80 per cent. alcohol. A crystalline precipitate is then rapidly deposited, consisting of hydrated sodium peroxide, which must be quickly separated from the liquid. The crystals, which are transparent flexible plates like mica, having a fine nacreous lustre and often of considerable size, have the composition $\text{Na}_2\text{O}_2 + 8\text{H}_2\text{O}$, and are identical with those which Harcourt obtained (v. 340) by spontaneous evaporation of an aqueous solution of sodium dioxide. When heated they give off 7 mols. H_2O and 1 at. O, and are converted into sodium hydroxide. In preparing them, care must be taken to keep the sodium hydroxide in excess, since an excess of hydrogen dioxide often completely prevents their formation (T. Fairley, *Chem. Soc. J.* xxxi. 126).

Sodium Monosulphide, Na_2S , is produced when a rapid stream of hydrogen sulphide is passed over fused sodium chloride: $2\text{NaCl} + \text{H}_2\text{S} = \text{Na}_2\text{S} + 2\text{HCl}$ (Klingzett, *Chem. News*, xxvii. 25).

On the Thermochemistry of the Sulphides of Sodium, see Sabatier (*Compt. rend.* lxxxix. 43; *Chem. Soc. J.* xxxvi. 865).

SOLANINE. This base has been represented by various formulæ. Zwenger a. Kind's analyses lead to the formula $\text{C}^{26}\text{H}^{41}\text{NO}^{16}$ (v. 346); according to Kletzensky (vi. 1030) it is $\text{C}^{21}\text{H}^{35}\text{NO}^7$. A. Hilger (*Liebig's Annalen*, exv. 317) from recent analyses assigns to it the formula $\text{C}^{26}\text{H}^{37}\text{NO}^{15}$, and to solanidine, obtained from it by boiling with dilute acids, the formula $\text{C}^{26}\text{H}^{41}\text{NO}^2$, but it is not easy to see how a compound of this latter formula can be formed, together with glucose, from solanine containing 42 atoms of carbon. Hilger finds that solanine, when thus decomposed, yields 35.7 to 36 per cent. glucose, whereas Zwenger a. Kind's equation (v. 347) requires 64 per cent. The subject evidently requires further examination. Both solanine and solanidine yield monoacetyl-derivatives (Hilger).

SONOMATITE. A sulphate of aluminium and magnesium from the Geyser-springs of Sonoma County, California. It is colourless, with a silky lustre, and has a density of 1.604. The following analyses have been made of it, leading to the formula $2\text{MgSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 33\text{H}_2\text{O}$:

SO^2	Al_2O^3	FeO	MgO	H^2O
38.78	7.66	2.01	7.14	44.41 = 100
38.30	8.36	1.56	7.51	44.27 = 100

(E. Goldsmith, *Zeitschr. Kryst.* i. 380).

SOPHORINE. An alkaloïd obtained from the pods of *Sophora speciosa*. It is liquid, and forms a stable chloride, which crystallises readily, and gives a deep red colour with ferric chloride. The base appears to be poisonous (H. C. Wood, *Pharm. J. Trans.* [3], viii. 1047).

SORBIC ACID, $\text{C}^{11}\text{H}^8\text{O}^2$. The tetrabromide of this acid, $\text{C}^6\text{H}^4\text{Br}^4\text{O}^2$, obtained by Barringer a. Fittig (vii. 1091), has been further examined by Kachel a. Fittig (*Liebig's Annalen*, clxviii. 276), who prepare it by mixing sorbic acid with about ten times its weight of carbon sulphide, and gradually adding the calculated quantity of bromine. Traces only of hydrobromic acid are then evolved, and the liquid, on standing for a day or two, deposits the tetrabromide in large well-formed crystals exhibiting the properties already described, or sometimes in globules of opaque needles.

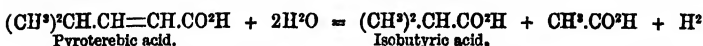
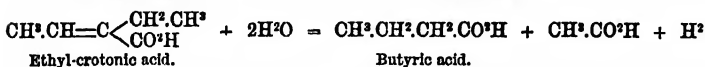
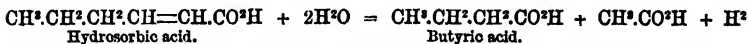
Sorbic tetrabromide, or tetrabromocaproic acid, forms well-defined salts. The sodium salt, $\text{C}^6\text{H}^4\text{Br}^4\text{O}^2\text{Na} \cdot 2\text{H}_2\text{O}$, forms magnificent silvery scales, easily soluble in water and in alcohol, but quite insoluble in a concentrated solution of sodium carbonate. The potassium salt is very soluble and difficult to obtain pure. It is not precipitated by the addition of potassium carbonate to its solution. The ammonium salt separates in fine needles from the solution of the tetrabromide in excess of ammonia. The barium salt, $(\text{C}^6\text{H}^4\text{Br}^4\text{O}^2) \cdot \text{Ba} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, may be formed by mixing barium chloride and the sodium salt. The calcium salt, $(\text{C}^6\text{H}^4\text{Br}^4\text{O}^2) \cdot \text{Ca} \cdot 7\text{H}_2\text{O}$, obtained in a similar manner, crystallises with great facility in fine large silvery scales. It is much less soluble in cold water than the barium salt, and makes its appearance even in somewhat dilute solutions. The zinc salt is similar in appearance to the barium salt.

These salts are decomposed by boiling with water, reproducing the tetrabromide, which separates in the form of a liquid afterwards becoming crystalline. A portion of the salt, however, undergoes further decomposition, and the hydrobromic acid liberated assists the separation of the tetrabromide, forming at the same time a corresponding quantity of sodium bromide.

When sodium hydrate or carbonate is added for the purpose of neutralising this hydrobromic acid as fast as it is generated, resinous products only are obtained; but, on substituting barium carbonate for the alkaline salt, a volatile highly irritating compound, probably acrolein, is produced, giving with ammoniacal nitrate of silver a reddish precipitate which deposits metallic silver on application of heat. The residue contains a small quantity of brown resinous matter, but no organic acid.

Sorbic Dibromide or *Dibromhydrosorbic acid*, $C^6H^4Br^2O^2$, is prepared like the tetrabromide, using however only one instead of two molecules of bromine, and remains, after the carbon sulphide has been removed by distillation, as a thick yellow oil, which gradually solidifies in a crystalline mass, to be purified by pressure and recrystallisation from petroleum-benzin. The dibromide thus prepared forms small shining crystalline laminae melting at 90° – 95° , easily soluble in alcohol, ether, and petroleum-benzin, less soluble in boiling water. It forms easily decomposable salts. Its alcoholic solution, mixed with alcoholic potash, yields a precipitate of potassium bromide.

Hydrosorbic acid, $C^6H^{10}O^2 = CH^3.CH^2.CH^2.CH=CH.CO^2OH$, metameric with ethyl-crotonic and pyroterebic acids, is formed by the action of water and sodium-amalgam on sorbic acid and on the tetrabromide (vii. 1091). When fused with potash, it is resolved, with evolution of hydrogen, into acetic and normal butyric acid, whereby it is distinguished from pyroterebic acid, which when similarly treated yields acetic and isobutyric acids. From ethyl-crotonic acid, which likewise yields normal butyric acid, it is distinguished by its physical properties, being liquid at ordinary temperatures, and not solidifying at -18° , whereas ethyl-crotonic acid is solid at ordinary temperatures, and melts at 41.5° . The formulæ of the three isomeric acids, and their modes of decomposition by melting alkalis, are represented by the following equations:



Action of Hydrobromic Acid on Sorbic and Hydrosorbic Acids (C. Stahl, *Ber.* ix. 120). Pulverised sorbic acid agitated with fuming hydrobromic acid dissolves completely, forming a clear liquid, and after a few hours there rises to the surface an oil which, after several days' standing and frequent agitation, sinks to the bottom and solidifies. The solution then yields well-defined nearly colourless crystals of dibromhexoic or dibromocaproic acid, $C^6H^{10}Br^2O^2$, which dissolves very easily in carbon sulphide, and by recrystallisation therefrom may be obtained pure and in colourless crystals. It melts at 68° , dissolves but very slightly in water, even at the boiling heat, and separates on cooling from a hot saturated solution as an oil which solidifies on addition of a trace of the solid acid. The acid is decomposed by prolonged boiling with water.

Hydrosorbic acid dissolves immediately in fuming hydrobromic acid, forming a clear solution, and after a short time an oily layer collects on the surface, its separation being complete in about three hours. This oil, after washing with water and drying over sulphuric acid, is nearly colourless, and consists of pure monobromocaproic acid, $C^6H^{11}BrO^2$. This acid does not solidify at -18° . It dissolves readily in dilute soda-ley, and the solution, if immediately treated with an acid, yields the bromocaproic acid unaltered; but after some hours acids separate nothing from it, and the acidified liquid yields on distillation, not bromocaproic, but hydrosorbic acid. From this cause also it yields, when treated with sodium-amalgam, not caproic but hydrosorbic acid (Stahl).

Pyroterebic acid, which is isomeric with hydrosorbic acid, does not unite with hydrobromic acid either at ordinary temperatures or when heated with it in sealed tubes (Fittig, *Ber.* ix. 1198).

SORDIDIN, $C^{14}H^{10}O^7$. A neutral crystallisable substance occurring, together with usnic acid and zeorin, $C^{13}H^{22}O$, in the lichen *Zeora sordida* (see ZKORA).

SPECTRAL ANALYSIS. I. EMISSION SPECTRA. a. Spectra of Metalloids. Nitrogen.—In the last Supplement to this Dictionary some experiments of Schuster were mentioned, which tended to prove that the baric-spectrum of nitrogen was due to an oxide. This idea was controverted by Salet (*Compt. rend.* lxxii. 665), who showed that nitrogen can be heated in contact with sodium or potassium, and yet give the spectrum in question. There is no reason now to doubt that the spectrum is really due to pure nitrogen.

Oxygen.—The spectrum of this element has recently been examined by Schuster (*Phil. Trans.* clxx. 1879, 37). Four spectra are distinguished.

1. The *Elementary Line-spectrum*.—This is the spectrum which appears at the highest temperature to which we can subject oxygen; that is, whenever the jar and air-break are introduced into the electric circuit. It consists of a great number of lines, especially in the more refrangible part of the spectrum. It has been called elementary line-spectrum to distinguish it from the other line-spectrum, because, according to one hypothesis which has been suggested to explain the variability of spectra, the molecule which gives this spectrum is in a simpler or more elementary state than that which gives the other so-called compound line-spectrum. We may, however, adopt the nomenclature independently of any hypothesis that may have suggested it.

2. The *Compound Line-spectrum*.—This spectrum appears at lower temperatures than the first. It consist of four lines: one in the red, two in the green, and one in the blue. With the exception of the blue line, all the lines in this spectrum widen very easily, and with an increase of pressure, more easily even than the hydrogen lines. They do not widen out equally on both sides, but more towards the red than towards the violet. This fact is especially noticeable in the more refrangible of the two green lines. The blue line always remains sharp.

3. The *Continuous Spectrum of Oxygen*.²—This spectrum appears at the lowest temperature at which oxygen is luminous. The wide part of a Plücker tube, filled with pure oxygen, generally shines with a faint yellow light, which gives a continuous spectrum. Even at atmospheric pressure this continuous spectrum can be obtained by putting the contact-breaker of the induction-coil out of adjustment, so that the spark is weakened. According to Becquerel, an excess of oxygen in the oxy-hydrogen flame produces a yellow colour, which is very likely due to this continuous spectrum. The continuous background which often accompanies the elementary line-spectrum must not be confounded with this spectrum.

The *Spectrum of the Negative Glow*.—This spectrum, which was first accurately described by Wüllner, is always seen in the glow surrounding the negative electrode in oxygen. It consists of five bands: three in the red, and two in the green. The least refrangible of the red bands is so weak that it easily escapes observation; the two other red bands are rather near together, and may be taken for one single band, if the dispersion applied is small. The two green bands, which appear of the same brightness throughout, with pretty sharply defined edges, are resolved into a series of lines, when looked at with high optical powers.

The following description of the appearance of a vacuum-tube filled with pure oxygen, as it undergoes gradual exhaustion, will give an idea of the way in which the spectra of oxygen gradually diffuse into each other:

At first the spark has a yellow colour, and the spectrum is perfectly continuous. Almost immediately, however, four lines are seen in the capillary part above the continuous spectrum. One of these lines is in the red, two are in the green, and one is in the blue. The discharge still passes as a narrow spark throughout the length of the tube. In the wide part the spectrum remains continuous, and it extends more towards the red and blue than in the capillary part. It seems as if the four lines had taken away part of the energy of the continuous spectrum. As the pressure diminishes, these lines increase considerably in strength, the spark spreads out in the wide part of the tube, and the intensity of the continuous spectrum is therefore considerably diminished, while it still forms a prominent part in the spectrum of the capillary part. When the pressure is small, the continuous spectrum decreases in intensity. At the same time, the negative glow, with its own characteristic spectrum, gradually extends through the negative half of the tube into the capillary part. The continuous spectrum has now entirely disappeared, and the bands of the negative pole and the four lines stand out on a perfectly black background. It is under these conditions that the change from the compound line-spectrum to the elementary line-spectrum is best studied. The mere insertion of the Leyden jar makes hardly any difference; the jar does not seem to be charged at all. If, in addition to the jar, we insert a movable air-break, which can be opened or closed at will, while we look through the spectroscope, we shall be able to see alternately two perfectly distinct spectra. If

the air-break is closed, the four lines of the compound-spectra only are seen; if the air-break is opened, these four lines will disappear entirely, and the elementary line-spectrum will come out. We have here as complete a transformation as we have from the band to the line-spectrum of nitrogen, taking place under exactly the same circumstances (*Phil. Trans.* clxx. 51).

Carbon.—The spectrum which is seen at the base of every candle-flame has lately given rise to a good deal of discussion. Attfield, Morren, Dibbits, Wüllner, W. M. Watts, and others had come to the conclusion that the spectrum was due to carbon and not to any hydrocarbon. Dibbits had furnished an answer to the theoretical difficulty that the spectrum of carbon should appear at so low a temperature. Before combustion, the carbon is combined with hydrogen; after combustion, it is combined with oxygen. It must therefore have existed during a certain stage of transition in the form of simple carbon uncombined. During this stage of transition it gives us the carbon-spectrum. In the year 1875, after Angström's death, Thalén published a paper in which he describes some experiments jointly made with Angström (*Nov. Act. Ups.* ix.) In consequence of these experiments, the authors expressed the opinion that the candle-spectrum was due to a hydrocarbon. The experiments which they gave in support of their view were made by taking the spark of carbon-electrodes in various gases, and examining the spectra of the 'auréole' or 'glory' as it might be called. If the spark is taken in oxygen, the undoubted spectrum of carbonic oxide appears; in hydrogen the candle-spectrum is seen; and in nitrogen some blue and violet bands are added to the candle-spectrum, which appear to be due to a compound of carbon and nitrogen. As it is known that acetylene is formed when the spark is taken in hydrogen, Angström and Thalén conclude that the spectrum seen in the 'glory' is due to acetylene.

Recently Liveing and Dewar have supported Angström's view (*Proc. Roy. Soc.* xxx. 152). They sum up that part of their work which relates to the candle-spectrum as follows:

In the next place, the green and blue bands, characteristic of the hydrocarbon flame, are well seen when the arc is taken in hydrogen; but, though less strong when the arc is taken in nitrogen or in chlorine, they seem to be always present in the arc whatever the atmosphere. This is what we should expect, if they be due, as Angström and Thalén suppose, to acetylene; for we have found that the carbon-electrodes always contain, even when they have been long treated in chlorine, a notable quantity of hydrogen. In the flames of carbon-compounds they by no means always appear; indeed, it is only in those of hydrocarbons or their derivatives that they are well seen. Carbonic oxide and carbon disulphide, even when mixed with hydrogen, do not show them; and if seen in the flames of cyanogen, hydrocyanic acid, and carbon tetrachloride mixed with hydrogen, they are faint, and do not form a principal or prominent part of the spectrum. This is all consistent with the supposition of Angström and Thalén.

Lockyer (*Proc. Roy. Soc.* xxx. 335) describes an experiment in which the bands in question were seen when the spark was taken in carbon tetrachloride, although no lines of hydrogen were visible. Those who believe the spectrum to be due to the element carbon rely chiefly on the brilliancy with which its bands are developed when cyanogen is burnt in oxygen; also when the spark is taken in cyanogen, carbon tetrachloride, and carbonic oxide at high pressure, all the gases being dried with the greatest care. Those who oppose this view, and who hold that the spectrum is due to a hydrocarbon, refer to the impossibility of excluding all traces of moisture, and to the fact that this spectrum is well developed under circumstances where we know hydrocarbons to be present.

Compounds of Carbon and Nitrogen.—A cyanogen flame shows, besides its own characteristic red and yellow bands, a series of flutings in the blue, violet, and ultra-violet. These bands have until recently been ascribed to carbon, as they were observed in carbon compounds not containing nitrogen, but according to experiments of Liveing and Dewar (*Proc. Roy. Soc.* xxx. 494), they can in those cases always be traced to impurities containing nitrogen. Thus, according to Watts, the bands are seen when a spark is taken in carbonic oxide at the atmospheric pressure. According to Liveing and Dewar this is true, if the carbonic oxide has been prepared from ferrocyanide of potassium. When, however, the gas was made by the action of sulphuric acid on dried formate of sodium, a faint trace of one of the bands only could be detected. When the gas was prepared by heating a mixture of quicklime with pure and dry potassium oxalate, no trace whatever of the bands in question appeared. Similarly, Watts and Lockyer had observed the bands in a tube containing carbon tetrachloride, but, according to Liveing and Dewar, these bands do not appear when the tetrachloride has been well purified, and when all traces of air have been expelled from the tube.

Chlorine, Bromine, Iodine.—Ciamician (*Wien. Ber.* [2], lxxviii, 872) has given an account of the successive changes which the spectra of these bodies undergo when the pressure is either greatly reduced or increased. Lines which are visible at one pressure disappear altogether, and are replaced by others when the pressure is changed.

b. Spectra of Metals. A most important contribution to our knowledge of the spectra of metals has appeared in Lecoq de Boisbaudran's 'Spectres lumineux' (Gauthier Villars, 1874). Lecoq de Boisbaudran has mapped the spectra of most metals as they appear when a spark is taken from a solution of the metallic salts. Not only is this method of great convenience to the chemist, who can generally obtain without difficulty a solution of the substance he wishes to examine, but it enables us also to observe metallic spectra at much lower temperatures than when the solid metal is used as pole; for a spark which is not sufficient to volatilise the metal will give a spectrum when taken from a metallic solution. We may also mention Rand Capron's 'Photographed Spectra,' a series of photographs of metallic, gaseous and other spectra, taken generally for each metal both with the arc and spark.

Bunsen (*Pogg. Ann.* clv. 366-384) has described the methods employed by him to detect erbium, yttrium, cerium, lanthanum, and didymium by means of their spectra. His paper is accompanied by plates giving the spectra obtained when a spark is taken from the chlorides of these elements.

Thalèn (*K. Vetrusk. Akad. Handl.* xii. No. 4) has also examined the spectra obtained from the chlorides of yttrium, erbium, lanthanum, and didymium, and given a list of their lines in wave-lengths.

During the year 1879, Nilsef announced the discovery of a new metal, 'scandium.' Thalèn has examined the spectrum of this metal, and found that it contained many characteristic lines. His final measurements will be found in the *Comptes rendus* (xci. 1880, 45). See YTTRIUM METALS.

It was explained in the last Supplement how Lockyer could, by means of his method of long and short lines, eliminate for each metal all lines due to impurities. An element present as an impurity made itself apparent by its longest lines, and hence it was assumed that, whenever the long lines of an element were present, they were due to an impurity. In his subsequent investigations, Lockyer (*Proc. Roy. Soc.* xxviii. 1878, 159) found that after the impurities had been eliminated by this method, there was still a large number of coincidences left between the lines of different metals. It was argued that the hypothesis that identical lines in different spectra are due to impurities is no longer sufficient to account for the fact, that therefore an additional hypothesis is needed, and that once we accept this additional hypothesis, even some of the long-line coincidences would find a better explanation by the new hypothesis. The new hypothesis Lockyer bases on the assumption that the elements are not simple bodies. Evidence is adduced that in the hottest stars hydrogen alone is present; that magnesium, sodium, calcium come in during the next stage; and that only when the temperature of the star has reached that of our sun, iron and the heavier metals are observed. If we assume the reason for these facts to be that part of the lighter elements enter into combination together to form the heavier metals, we should explain the short-line coincidences. Lockyer supports his views by the behaviour of some metals when exposed to different temperatures. Thus calcium (*Proc. Roy. Soc.* xxiii. 1876, 352) in the flame or in a very weak spark shows only the blue line. In the arc the two violet lines (H and K) make their appearance. As the power of the arc or spark is increased, the violet lines gain relatively in strength, and finally the blue line disappears altogether. The spectrum of iron behaves in a remarkable way; the relative intensity of the lines varying much according to circumstances. In solar storms weak iron lines are often seen, while some of the strong ones appear much more seldom. In two subsequent papers, Lockyer (*ibid.* 1878; xxix. 1879, 247) follows out the solar evidence, discussing the lines seen by Young in the solar chromosphere. Maps are given, showing for each line the frequency with which it has been seen by Young and the intensity as given by Thalèn. The two quantities, as it appears, are by no means identical. The question is discussed whether the lines most often seen in solar storms and in spots are those which are common to two or more metals, and Lockyer concludes that they are.

Some remarkable phenomena are mentioned by Lockyer in a further communication to the Royal Society (*Proc. Roy. Soc.* xxix. 1879, 266). A spark is passed through a vacuum tube; below one electrode a piece of sodium is gradually heated. At first a yellow glow is seen between the electrode and the metal, the glow giving the yellow sodium line. As a greater quantity of sodium-vapour is volatilised, the yellow glow rises, and a brilliant leaf-green glow now adjoins the metal. The leaf-green glow

gives the red and green lines of sodium without the yellow lines. In a similar way, the yellow-green lines of potassium could be seen without the red.

c. Spectra of Compound Bodies. An important communication on the spectrum of the flame of hydrogen was sent on June 16, 1880, to the Royal Society by Mr. Huggins (*Proc. Roy. Soc.* xxx. 1880, 576). Photographs of the spectrum given by a non-luminous flame of hydrogen showed a strong series of bands in the ultra-violet lying between wave-lengths 3062 and 3276. This spectrum is in all probability a spectrum of water. The spectrum was also found to be present in the blue cone of an ordinary blowpipe flame. Liveing a. Dewar (*ibid.* xxx. 1880, 580) independently discovered the same spectrum, and found it to be present when a spark was taken in moist gases.

In the year 1878, Liveing a. Dewar (*ibid.* xxviii. 368, 474) mentioned that a spark taken between magnesium poles in hydrogen showed some lines which were not present when the spark was taken in an atmosphere of nitrogen or carbonic oxide; they ascribe the spectrum to a combination of hydrogen and magnesium. Their first communication left it rather doubtful whether the line was not simply due to the lower temperature of the spark in hydrogen, but the more detailed account of their experiments (*ibid.* xxx. 1880, 93) leaves no reasonable doubt that the presence of hydrogen is necessary to the formation of this spectrum.

Liveing a. Dewar (*ibid.* xxviii. 1879, 352) discovered a band 5700 to 5175 which seems to be due to a compound of potassium and carbonic oxide.

The *Proceedings of the Cambridge Philosophical Society* (iii. 96) contains a drawing of the spectrum of calcium fluoride obtained when a fluor moistened with hydrochloric acid is heated in the flame of a Bunsen burner. The drawing differs somewhat from that given of the same spectrum by Mitscherlich (*Phil. Trans.* clxvii. 1876, 207).

As regards some theoretical questions, especially with regard to the formation of double spectra, we must refer to two papers by E. Wiedemann (*Wied. Ann.* v. 500; viii. 202), who has described in the latter paper some experiments made for the purpose of deciding whether heat is absorbed or given out the moment a gas changes its spectrum. In the case of hydrogen it was indeed found that an absorption of heat took place when the band-spectrum changed into the line-spectrum, and that the amount is independent of the cross-section of the vacuum-tube containing the hydrogen, and also of the pressure. Unfortunately the band-spectrum of hydrogen is one of doubtful origin, many spectroscopists ascribing it to an impurity of hydrocarbons. Wiedemann will, however, no doubt extend his observations to other gases which possess undoubted double spectra.

II. ABSORPTION-SPECTRA

a. Absorption-spectra of Vapours. We have had in the last few years three maps of the absorption-spectrum of bromine. One by Roscoe a. Thorpe (*Phil. Trans.* clxvii. 1876, 207), one by Moser (*Pogg. Ann.* clx. 1877, 177), and apparently the best and most accurate one by Hasselberg (*Mém. de St. Pé.* xxvi. 1878, 4). Roscoe a. Thorpe's map extends, however, further into the red than the other two. Moser investigated the changes seen in the spectrum when the vapour is heated. Some of the bands seem to disappear and to be replaced by others. Hasselberg, in the same paper, gives us a very accurate set of measurements of the absorption-spectrum seen when white light is sent through the vapour of nitrogen tetroxide. Moser also investigated the changes in this spectrum, and finds that three bands near C disappear at a high temperature. It seems likely that these bands are due to the more complex molecule N_2O_4 which we know to be broken up when the temperature is raised.

The absorption-spectra of metallic vapours were examined by Liveing a. Dewar, and the results were communicated in a series of papers to the Royal Society (*Proc. Roy. Soc.* xxvii. 132, 350, 494; xxviii. 352, 367, 471; xxix. 402). At first the substances were heated up in an iron tube, and the continuous spectrum sent out by the tube was used as background against which the reversals were observed. In order to obtain higher temperatures, the iron tube was replaced in the later experiments by crucibles of lime or carbon, and the substances were heated either in a jet of the oxyhydrogen flame or later by means of the voltaic arc derived from a dynamo-electric machine. The following is a short summary of the results which were obtained:

Sodium.—In the iron tube the channelled spaces described by Roscoe a. Schuster were seen, but it was pointed out that the green line (5510) was not coincident as assumed by them with the double green sodium line. In the later experiments with higher temperatures, all the lines except one pair given by Thalén as belonging to

sodium were seen reversed, and the order in which they appeared was as follows: The double yellow line, the pair at 5687, the pair at 4983, the pair at 4670, and finally the double red line at 6160. It is curious that the pair at 5154 has not been seen reversed. The pair at 4670 is not given by Thalén at all, but by Lecoq de Boisbaudran. A mixture of magnesium and sodium gave a band at 5300, which was seen only in this mixture.

Potassium.—In the iron tube the channelled spaces appeared in the green; but those in the red observed by Roscoe a. Schuster were not seen. There can be little doubt however that they do exist and really belong to potassium. The dark line at 5730, Liveing a. Dewar proved not to be identical with the potassium line near it, as assumed by Roscoe a. Schuster. No line of potassium was reversed in the iron tube; but a mixture of potassium and magnesium gave two dark lines in the red (6580, 6475) which could not be traced either to potassium or to magnesium, but appear only when the two metals are present together. At higher temperatures the lines of potassium make their appearance.

Lithium.—Lithium gave no results in the iron tube, but when the chloride was introduced together with metallic sodium and potassium, the red line was seen reversed. At higher temperature the green line was seen reversed.

Rubidium.—Rubidium chloride heated in a glass tube with sodium shows the reversal of the two violet lines. At higher temperature the less refrangible of the two red rays is also reversed.

Cesium.—Cesium chloride heated in a glass tube showed the two blue lines.

Magnesium showed in the iron tube in an atmosphere of hydrogen the reversal of 6, and the spectrum which has been already mentioned was traced to a compound of magnesium and hydrogen. At higher temperatures the other metallic lines appear, with the exception of 4481, which was not seen, but on the other hand a new line at 4354 was seen reversed.

In a similar way the absorption-spectra of the vapours of barium, calcium, strontium, silver, gallium, lead, zinc, cadmium, bismuth, copper, iron, and manganese are described.

Absorption-spectra of Liquids. The study of the absorption-spectra of liquids is daily gaining more importance. As, however, the absorption-spectrum of a salt often varies with the solvent, and even with the presence of other bodies, great care is necessary when the spectroscope is used in qualitative analysis. In some cases, however, the instrument may give much information. H. W. Vogel (*Ber. d. Chem. Ges.* 1876, ix. 1641), for instance, shows how small traces of alumina or magnesia may be traced in solutions. For this purpose Vogel makes use of the action of purpurin on these bodies. An alcoholic solution of purpurin shows an absorption over F and one between 6 and E. If the solution is alkaline, a band appears between E and D; this is to be avoided, which can be done by adding a small quantity of lime-water to the solution. If to this solution a liquid containing small quantities of an aluminium salt is added, two very characteristic bands appear, one between E and D and one between F and 6. Salts of magnesia show bands in nearly the same position, but magnesia bands disappear on addition of a drop of acetic acid, while the bands which are due to alumina remain. Vogel (*ibid.* 1875, 1533) also shows how manganese, chromium, cobalt, uranium, and iron can under certain circumstances be recognised by means of the spectroscope.

Chromium compounds. Erhard has subjected some of the salts of chromium to a careful investigation. He describes the absorption-spectrum of crystals of chromium-potassium sulphate, and finds it to be identical with that of chromium ammonium sulphate. It is characterised by some absorption-bands in the red more refrangible than C. The remainder of the spectrum is the same as that of the solutions of the salt, exhibiting strong continuous absorption in the blue, but partial transmission of the violet. Chromic chloride differs from the other salts by transmitting light between E and G. The red oxalate of potassium and chromium transmitted only the red. The blue oxalate gave an absorption band in the red, and transmitted some of the blue and violet.

The absorption-spectra of the solutions of the alums, of chromium sulphate, and of the chloride and nitrate resemble each other, and transmit more light than a solution of the oxalates, tartrate, and acetate. Professor Soret has paid some attention to the absorption-spectra of the chromates (*Archives sc. phys. Nat.* 1878, lxi. 322), and has traced them into the ultra-violet by means of his spectroscope with fluorescent eyepiece. He finds the spectra of the chromates of potassium, sodium, and ammonium, of the diluted bichromates of potassium and ammonium, to be identical. Chromic acid showed the same spectrum less distinctly.

Discovery of new elements. The spectroscope has played an important part in the discovery of some new earths from the minerals gadolinite and samarskite. Marignac had been led to the discovery of a new element which he called *ytterbium*. He gave some of his preparations to Soret, who after examination came to the conclusion that at least one other element was present besides (*Compt. rend.* 1878, lxxxvi. 1062). This element gave some very characteristic bands, especially in the ultra-violet. The bands were not due either to any previously known elements, or to the newly-discovered ytterbium, which gives no characteristic absorption-bands (its emission-spectrum was mapped by Lecoq de Boisbaudran; *Compt. rend.* 1879, lxxxviii. 1342). This new element Soret only called X, as he considers it to be identical with one the discovery of which had been announced by Delafontaine, to whom he consequently left the choice of a name. Subsequent researches have confirmed this supposition, and the element was named by its discoverer *philippium*. Clève independently discovered its existence by means of the spectroscopic evidence, and called it *holmium*, but afterwards acknowledged Soret's priority.

Soret, and after him Clève, also found some remarkable variations in the intensity of a red absorption-band ($\lambda = 684$), and suggested the possibility of the existence of a distinct element, for which the name of *thulium* was suggested by Clève; Soret, however, who has the priority of the discovery, did not consider the evidence sufficiently strong as yet to justify his giving any name to this element, the existence of which though probable is not proved.

Delafontaine (*Compt. rend.* 1878, lxxxvii. 632) also thinks he has obtained conclusive evidence of the existence of another earth, *decipium*, which is characterised by two bands ($\lambda = 416$ and $\lambda = 478$), and Lecoq de Boisbaudran (*ibid.* 1879, lxxxix. 212) has obtained an absorption-spectrum which he considers to be due to an element different again from decipium, which he calls *samarium*. It seems certain that the products examined by Delafontaine and Lecoq de Boisbaudran contain a new substance, but also that they contain something in common. Whether samarium is identical with decipium, or whether they are mixtures in unequal quantities of a new body with a known one, or of two new bodies, it is as yet impossible to say.

Relationship between different spectra. We have to note some important investigations on the question whether an element preserves its absorbing properties when combined with another, and whether substances having a similar chemical constitution present analogies in their spectra. Gladstone and Miller had previously given their attention to this question, and found that acids and bases preserved their absorbing powers when combined together. This result has been confirmed by Soret (*Arch. sc. phys. Nat.* 1878, lxi. 322), who finds that, if acids transparent to the ultra-violet rays combine with transparent bases, the compound is also transparent; but an acid which absorbs certain parts of the spectrum will also absorb it when combined with a transparent base. A very curious confirmation of this law is derived from a study of nitric acid and the metallic nitrates, which all begin to absorb the ultra-violet rays at the same limit, and have a maximum of absorption for a wave-length of about 3000 tenth metres. More recently Soret has examined, jointly with Rilliet (*Compt. rend.* 1879, lxxxix. 747), the absorption-spectra of the alcoholic nitrates and nitrites, and finds that, although the place where the general absorption begins is much the same as in the metallic salts, nevertheless some of the characteristic properties disappear. Hence Soret and Rilliet conclude that the alcoholic nitrates have a chemical constitution different from that of the metallic salts.

Hartley and Huntington (*Phil. Trans.* 1879, clxx. 257), in a long and careful work, have examined the question of relationship of spectra in similarly constituted bodies. They have arrived at the following conclusions:

(1). The normal alcohols of the series $C^mH^{2m+1}OH$, are remarkable for transparency to the ultra-violet rays of the spectrum, pure methylic alcohol being nearly as much so as water.

(2). The normal fatty acids exhibit a greater absorption of the more refrangible rays of the ultra-violet spectrum than the normal alcohols containing the same number of carbon-atoms.

(3). There is an increased absorption of the more refrangible rays corresponding to each increment of OH^2 in the molecule of the alcohols and the acids.

(4). Like the alcohols and acids, the ethereal salts derived from them are highly transparent to the ultra-violet rays, and do not exhibit absorption-bands.

They have also examined substances containing the benzene-nucleus, and obtained the following results:

(1). Benzene, and the hydrocarbons, alcohols, acids, and amines derived therefrom are remarkable—first, for their powerful absorption of the more refrangible rays; secondly, for the absorption-bands made visible by dissolving them in water or

alcohol; and thirdly, for the extraordinary intensity of these absorption-bands—that is to say, their power of resisting dilution.

(2). Isomeric bodies containing the benzene-nucleus exhibit widely different spectra, inasmuch as their absorption-bands vary in position and in intensity.

(3). The photographic absorption-spectra can be employed as a means of identifying organic substances, and as a most delicate test of their purity. The curves obtained by co-ordinating the extent of dilution, or, in other words, the quantity of a substance, with the position of the rays of the spectrum transmitted by the solution, form a strongly-marked and highly characteristic feature of very many substances.

Hartley has since extended his experiments, and seems to have come to the conclusion that no carbon-compound will give distinct absorption-bands unless it contains three pairs of carbon-atoms doubly linked together.

Influence of the Solvent on the Position of Absorption-bands.—Kundt discovered that, if a body showing characteristic absorption-bands is dissolved in different liquids, the bands are sometimes slightly shifted towards one or the other end of the spectrum. In his latest and most complete investigation (*Wied. Ann.* 1878, iv. 34) he examined chlorophyll, aniline green, cyanine, fuchsine, quinzarin, and the yolk of egg, dissolving these bodies in the following substances: methylic alcohol, water, ether, acetone, ethyl alcohol, amyl alcohol, chloroform, benzene, toluene, oil of cassia, and bisulphide of carbon. The general result was that if two solvents have diffusive powers which differ much, the one with the greater dispersion will show the absorption-band displaced towards the red. If the liquids have approximately equal dispersive powers, the results are not the same for all bodies, and no general rule can be given. A paper by Clees (*ibid.* 1878, iii. 389) will also give some useful experimental facts, but his discussion is vitiated by a serious error in the theoretical part.

III. APPLICATION OF SPECTRUM ANALYSIS TO ASTRONOMY.

Owing to the calm state of the solar surroundings in the last few years, solar physics has not advanced so rapidly as it otherwise would have done. Considerable progress has however been made in some of its branches. We have had several new maps of the solar spectrum. In the visible part, Dr. H. C. Vogel, of the Potsdam Observatory, has in the first publication of that institution given a map on a larger scale than Angström's, reaching from the green into the violet. Prof. Piazzi Smyth (*Trans. Roy. Soc. Ed.* xxix. 285) has also carefully remeasured the visible part of the solar spectrum from A to H. He does not give a map, but gives symbolical representations of the appearance of each line, together with its measurement, which is reduced to wave-numbers in British inches; that is, the number of waves contained in a British inch. Cornu (*Ann. Ec. Nom.* iii. 421, ix. 21) has taken comparisons of the ultra-violet regions of the solar spectrum with the metallic lines, and he has carefully drawn up a map of Angström's scale of wave-lengths. Most of the ultra-violet lines which have been identified by him belong to iron and nickel, but some also to manganese, magnesium, and sodium. Abney (*Proc. Roy. Soc.* xxx. 67) has succeeded in preparing silver bromide which absorbs the red and ultra-red rays, and is sensitive to these rays. In the Bakerian Lecture for 1879, Abney has explained his methods (the full paper will appear in the forthcoming volume of the *Philosophical Transactions*) and the apparatus by means of which he has been able to obtain photographs of the spectrum as far as $\lambda = 10730$ tenth metres, thus extending our knowledge of the solar radiation through nearly a whole octave.

Two total eclipses of the sun, one in 1875 and one in 1878, fell into a time where sun-spots were very rare and the solar corona in a very quiet state. The first, mentioned eclipse was observed in Siam (*Trans. Roy. Soc.* 1878, Part I.) Photographs were obtained of the corona, which was symmetrical, round an axis nearly, if not entirely, coinciding with the solar axis. Photographs were also taken with a camera having a prism placed in front of the object-glass. The image of the corona was drawn out into a band showing that nearly the whole of its light gave a continuous spectrum. The prominences, on the other hand, gave distinct images corresponding to the hydrogen line F and near G. The strongest image, however, was in the extreme violet, near H. This image was very likely due to a hydrogen line, which has since been discovered to coincide with H. The eclipse of 1878 was observed by many astronomers in America. Photographs of the corona were taken by the Washington observers, which will most likely prove to be more perfect than any we have hitherto possessed. The corona much resembled that of 1875. Its spectrum was chiefly continuous, the bright green line not being very conspicuous. Draper's party observed the dark Fraunhofer lines in the spectrum of the corona.

Considerable interest was aroused by Draper's (*Amer. Phil. Soc.* 1877) announce-

ment that he had discovered, by means of photography, bright lines in the violet part of the spectrum, which corresponded with the bright lines of the oxygen. Copies of his photograph accompanied the paper. Just those observers, however, who were accustomed to work with instruments of greater power than those generally in use, felt rather doubtful as to Draper's conclusions. The existence of bright lines in the solar spectrum has often been mentioned. But when such an apparently bright line is examined with instruments of high power, it is generally found to be due to an effect of contrast. Dark lines closely ruled together, which could not be resolved with the lower dispersion, now appear on either side. These dark lines fuse together if the dispersion is insufficient, and make the interval between them appear brighter than the general background. It was and still is held by several observers (Christie, *Monthly Notices, R. A. S.*) that Draper's bright lines are due to this cause. It must however be urged, on behalf of Draper, that, granting the existence of these bright lines, it is quite possible that they should come out better with smaller dispersive powers; for the lines of oxygen we know would not be sharp, and high powers might easily draw them out into bands of such width and decreased intensity that we might not fail to detect them. Draper (H. C. Vogel, *Observations at the Potsdam Observatory*, vol. I.) has since his first publication repeated his experiments with more powerful apparatus, and his photographs obtained have convinced many observers, whose opinion is entitled to much weight, of the justness of his conclusions. But the question will most likely not be settled to the general satisfaction of spectroscopists until photometric measurements have shown that these bands are really brighter than the other parts of the spectrum.

An important step has been made by Huggins, who has succeeded in obtaining admirable photographs of the spectra of some of the stars. The following quotation (*Proc. Roy. Soc.* xxx. 21) will show the extent and some of the results of the work.

'Photographs have been obtained of the stars Sirius, Vega, α -Cygni, α -Virginis, η -Ursæ Majoris, α -Aquilæ, Arcturus, β -Pegasi, Betelgeux, Capella, α -Herculis, and α -Pegasi; also of the planets Jupiter, Venus, and Mars, and of the different parts of the moon.

'The spectra of Sirius, Vega, α -Cygni, α -Virginis, η -Ursæ Majoris, α -Aquilæ, and Arcturus, are laid down in a map on the scale of Cornu's map of the ultra-violet part of the solar spectrum.

'The stellar spectra extend from about G to O in the ultra-violet. The stars of the white class are arranged so as to exhibit, first, the remarkable spectrum typical of this class, and then some of the modifications it appears to undergo.

'The typical spectrum of this region of this class consists of twelve strong lines winged at the edges. The continuous-spectrum extends in the photographs beyond S, but no lines are seen more refrangible than the twelfth line 3699. Two of these lines agree in position with the hydrogen line (γ) 4340, and the other line at h . The third line agrees with H_1 . The remaining nine form a group, in which the distance between any two adjacent lines is less as the refrangibility increases, suggesting that they are connected with each other and represent probably one substance.

'A very suggestive modification presents itself in the difference of the character of the line H_2 . In these stars this line is either absent or very thin as compared with its appearance in the solar spectrum. In the spectrum of Arcturus, which belongs to the solar type, this line exceeds in breadth and intensity its condition in the solar spectrum. The white stars may, therefore, be arranged in a series in which the line H_2 passes through different stages of thickness, at the same time that the typical lines become narrower and more defined, and other finer lines present themselves in increasing numbers. Arcturus seems to present a spectrum on the other side of that of the sun in the order of change from the white-star group.'

H. W. Vogel (*Nature*) has taken photographs of the spectrum of hydrogen, and has been able to identify several of the lines which appear on Huggins' photographs of the spectra of white stars with hydrogen lines, especially the line which is apparently coincident with H_1 .

A. S.

SPERGULIN. A fluorescent body, occurring in the seed-coverings of *Spergula vulgaris* and *S. maxima*, and produced at the time when the seeds blacken and are nearly ripe. It has not been obtained in crystals. It is very soluble in ethyl alcohol, both anhydrous and aqueous, also in methyl alcohol, less soluble in amyl alcohol, nearly insoluble in ether and in petroleum. Strong sulphuric acid dissolves it, forming a dark blue liquid. Its solution in common alcohol, when viewed by transmitted light, appears nearly colourless with a shade of olive-green, but by reflected light it exhibits an intense dark-blue fluorescence, which remains permanent more than a year if the liquid be kept in darkness, but is rapidly destroyed in sunshine, and more

slowly in diffused daylight. Small quantities of alkalis and alkaline carbonates added to the alcoholic solution transform the spergulin into a body exhibiting an emerald-green fluorescence; the alcoholic solution gives a precipitate with acetate of lead. An alcoholic solution of spergulin (1 : 8) exhibits strong absorption, almost wholly in the violet, differing considerably in this respect from chlorophyll, phyllocyanin, and phylloxanthin.

Spergulin gives by analysis 61.85 per cent. carbon and 7.06 hydrogen, agreeing approximately with the empirical formula $C^6H^2O^2$. It appears to be related to chlorophyll, and is perhaps closely allied to phyllocyanin. It may be regarded as a weak acid which exhibits blue fluorescence in the free state and in its acid salts, green fluorescence in its neutral salts, and none at all in its basic salts (C. O. Harz, *Chem. Centr.* 1879, 24).

SPESSARTIN. A variety of garnet from St. Marcel in Piedmont (p. 846).

SPHÆROCOBALTITE, or *Cobalt-spar*, is a native carbonate of cobalt belonging to the calc spar-group, black on the outside, red within; occurring, together with rosasite, in the Daniel Mine near Schneeberg. After deducting the iron as limonite, the analytical values (A) lead to the formula $CoCO_3$, the numbers calculated from which are given under B :

	CoO	CaO	Fe ² O ³	CO ²	H ² O	
A.	58.86	1.80	3.41	34.65	1.22 =	99.94
B.	63.06	—	—	36.94	— =	100

(C. Winkler, *J. pr. Chem.* [2], xvi. 89). By examination with the microscope, A. Weisbach found the small spherical masses to consist of rhombohedral crystals R. O. R. Sp. gr. = 4.13 (*Jahrbuch f. Min.* 1877, 409).

SPHÆROLITE. A volcanic glass from the lava of Antisana (sp. gr. 2.386) analysed by G. vom Rath (*Zeitschr. geol. Ges.* xxvii. 295), with the following results :

SiO ²	Al ² O ³	Fe ² O ³	CaO	MgO	K ² O, Na ² O	H ² O
77.01	12.90	1.88	0.21	0.29	7.26	0.45 = 100

SPHÆROSIDERITE. This mineral occurs in a tertiary clay at Stein in Carinthia, in small globules mixed with sand, and containing, besides traces of manganese, water, and organic substance :

FeCO ³	Fe ² O ³	CaCO ³	MgCO ³	Insoluble
72.96	2.03	9.68	3.18	11.94 = 99.79

(F. Ullik, *Min. Mitth.* 1873, 231).

Manganiferous sphærosiderites from Hungary have been analysed by Schröckinger a. Dietrich (*Min. Mitth.* 1877, 114).

1-3. From Felsöbanya : dirty-white or yellowish-brown globules, on antimony-glance or heavy spar. 4. From Kapnik : grey or yellowish stalactites with concentrically scaly texture :

FeCO ³	MnCO ³	CaCO ³	MgCO ³	H ² O	
53.07	44.36	1.15	1.49	— =	100.07
46.64	38.07	9.96	4.78	— =	99.45
62.12	27.76	7.05	2.41	— =	99.34
56.84	39.84	0.55	1.29	0.67 =	99.19

SPIAUTERITE. A variety of zinc sulphide. See ZINC.

SPIEGELEISEN. Manganiferous cast-iron, in which the proportion of manganese does not exceed 26 per cent. See IRON METALLURGY (pp. 1108-1111).

SPINEL. The spinel of Tiriolo in Calabria is opaque, dark greenish-blue, faintly lustrous, and brittle with irregular fracture. Sp. gr. = 3.7 at 12°. Its analysis gave :

Al ² O ³	ZnO	MgO	FeO	Sb ² O ³	
63.64	21.28	12.34	4.53	0.34 =	102.13

agreeing nearly with the formula $(Zn,Mg,Fe)_3Al_2O^4$ (Munro, *Gazz. chim. ital.* ix. 70).

Spinel occurs abundantly in the dolomitic limestone of Svinetic in the Böhmerwald (Helmhacker, *Min. Mitth.* 1873, 275).

On pseudomorphs of Spinel after Corundum, see CORUNDUM (p. 570).

Artificial Formation.—J. Aumann (*Chem. News*, xxxviii. 108) has obtained crystals of magnesium aluminate, $MgAl_2O^4$, in regular octohedrons which scratched glass readily, by igniting magnesia packed in a crucible of hard carbon and having a lump of aluminium imbedded within it.

SPIRÆA. According to Nietzki (*Arch. Pharm.* [3], iii. 429), the ethereal oil

of meadow-sweet (*Sp. ulmaria*) contains not salicylic aldehyde as stated by Wicke (v. 187), but a mixture of a hydrocarbon with a salicylic ether, probably methyl salicylate.

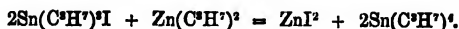
SQUILL. On the Carbohydrate obtained from this plant, see SINISTRIN (p. 1802).

STÄDELER'S BLUE. Städeler obtained this colouring matter by heating 1 mol. azobenzene with 2 mols. aniline hydrochloride at 170° – 230° (vi. 270). A similar compound, having the composition of triphenylene-diamine, $C^{19}H^{12}N^2$, is produced, together with sal-ammoniac, by heating 2 mols. aniline with 1 mol. nitrobenzene and dry hydrochloric acid in sealed tubes for six hours at 230° ; also by heating diphenylamine with nitrobenzene and dry hydrochloric acid at 230° , and by the action of dry hydrochloric acid on azodiphenyl blue at 216° .

STANNOISOBUTYL-COMPOUNDS. See BUTYL-COMPOUNDS (p. 358).

STANNOPROPYL-COMPOUNDS. A number of these compounds, obtained by Cahours, have already been described (vii. 1014).

Stannotetrapropyl, $Sn(C^3H^7)^4$, is prepared by heating stannotripropyl iodide with zinc-propyl:



When separated from the product by potash-solution, it forms a colourless mobile liquid, having a pungent ethereal odour, a density 1.179 at 14° , and boiling at 222° – 225° . When gently heated with nitric or sulphuric acid, it is strongly attacked, with formation of crystallised products, probably salts of stannotripropyl (Cahours, *Compt. rend.* lxxvi. 133).

STARCH, $nC^6H^{10}O^5$. On the formation of Starch in Chlorophyll-granules, see PLANTS (p. 1644).

On the occurrence of Starch in Egg-yolk, see EGGS (p. 704).

Composition of the Starch-granule (Brown a. Heron, *Chem. Soc. J.* xxxv. 610). Starch-granules are built up of distinctly stratified layers, mainly consisting of a substance designated by C. Nägeli * as granulose. The outer layers are for the most part denser than those nearer to the nucleus, and increase from without inwards in the amount of water which they contain. Every part of the granule contains, besides granulose, a small quantity of another substance, very closely allied to granulose, and distinguished by recent observers as starch-cellulose. The outer layers, which consist mainly, if not wholly, of this latter substance, are the oldest in point of growth, the starch-granule increasing by intussusception, i.e., the formative material, absorbed from without during the growth of the starch-grains within the protoplasm of the plant cell, is deposited between the already existing particles in the direction of the surface of the layers (Nägeli). To the presence of this protective coating of cellulose is to be attributed the fact that starch-granules when intact are absolutely unacted upon by cold water. Although water is absorbed to a very large extent by the granulose, none of this substance, which is to the highest degree colloidal, is able to diffuse into the surrounding medium. When, however, the outer layer of the granule is ruptured by attrition, the contents become much swollen from absorption of water, and a small quantity of matter having all the properties of *soluble starch* goes into solution. By repeated treatment of the ruptured starch-grains with cold water, the greater part of the granulose may be removed, most of the cellulose being left behind in the form of extremely thin layers, which, unlike the granulose, acquire, when treated with iodine, only a dirty yellow colour. Granulose itself, and water which has been only for a short time in contact with it, are coloured deep indigo-blue on addition of a solution of iodine. Fr. Schulze (Henneberg's *Journ. Landwirth.* New Ser. vii. 214) has obtained starch-cellulose by digesting starch for several days at 60° with a saturated solution of common salt containing 1 per cent. of hydrochloric acid. Nägeli also obtained the same substance by acting on starch at 45° – 55° with saliva, which contains an active agent (ptyalin) capable of attacking and dissolving only the granulose. Lastly, Fitz (*Ber.* x. 282) has recently observed that certain schizomycetes easily ferment the granulose of starch-paste, but leave the starch-cellulose unattacked.

The action of malt-extract on starch-paste in the cold affords a ready means of obtaining the cellulose of the starch-granule in large quantities. When a starch-paste containing from 5 to 6 grams of starch per 100 c.c. is treated, when quite cold, with about one-tenth of its volume of freshly prepared normal malt-extract, the mixture becomes perfectly limpid in from four to eight minutes, and can then be easily filtered. The flocculent matter left on the filter, after being freed from malt-extract and the

* *Die Stärkekörner.*

products of transformation of the granulose, by washing with cold water, consists of the so-called starch-cellulose. The filtered liquid, at first perfectly bright, becomes turbid in a few minutes from the separation of a further quantity of flocculent matter, which does not appear to differ, except in want of structure, from that previously separated by filtration. This further separation of cellulose is due to the fact that the soluble starch and the higher dextrins, the first products of the action of malt-extract upon granulose, are capable of holding some of the cellulose in solution; as the soluble starch and the higher dextrins are broken up, most of this separates in the insoluble form. The matter left upon the filter consists of fine laminae still retaining the shape of the swollen starch-granules, whilst the precipitated portion is amorphous.

Starch-cellulose after separation in this way is perfectly insoluble both in cold water and in water at 70°–80°, also in solutions of soluble starch or of the higher dextrins. That it is capable, under certain conditions, of entering into solution is shown, however, by the facts mentioned above, and by the impossibility of preparing it with a very dilute starch-paste, i.e., 1 to 1.5 gram per 100 c.c.*

Insoluble starch-cellulose is not acted upon by malt-extract in the cold, or at a temperature of 60°; the soluble modification appears, however, to be acted upon by malt-extract, somewhat slowly indeed in the cold, but rapidly at temperatures from 50°–70°.

Boiling with water converts starch-cellulose to a great extent into soluble starch, the solution having all the optical properties of that body, and yielding the characteristic indigo-blue reaction with iodine. After repeated boiling with water and frequent washing, there is left a body upon which a continuation of this treatment has no further effect. This body, amounting to about one-fifth of the original substance acted upon, is readily soluble in a solution of potash, under the action of which it is slowly converted into soluble starch on digestion at an elevated temperature.

Insoluble starch-cellulose evidently consists of at least two substances, one readily acted upon by boiling water, and the other not. Both these bodies must be very closely allied to granulose, since all these substances, under favourable conditions, yield soluble starch as the first product of their transformation.

When starch-cellulose is dissolved in liquid potash-solution, the greater part of it can be reprecipitated by the addition of acetic acid, or by passing carbon dioxide into the liquid. If the alkaline solution is kept at ordinary temperatures and reprecipitated immediately with acid, about 30 per cent. is found to have been converted into soluble starch. If the solution is digested at a moderately elevated temperature, precipitation with acid indicates the formation of a larger quantity of soluble starch. In one case digestion for half an hour at 60° resulted in the recovery of only 57.3 per cent. of the original quantity of cellulose.

The specific rotatory power of an alkaline solution of starch-cellulose appears to be very variable, but always increases on digestion at a high temperature. The specific rotatory power of a freshly prepared solution, calculated on the quantity of carbohydrate present, is sometimes as low as $[\alpha]_D = 146^\circ$, but increases on digestion for a few minutes at 60° to $[\alpha]_D = 173.6^\circ$. The rise of angle under these conditions is due to the conversion of cellulose into soluble starch. The entire optical activity of the solution cannot, however, be due to the presence of this latter substance; the cellulose itself must, when held in solution with potash, exert some effect upon polarised light.

When potato-starch is transformed under the influence of malt-extract at temperatures above 45°, cellulose separates out only when the paste is of a high degree of consistency, and the malt-extract is deficient in quantity: hence it is evident that starch-cellulose, at the moment of its separation from granulose, must under these circumstances be readily soluble.

Starch-paste.—When starch is treated with hot water, the contents of the granules, owing to a large absorption of water, swell up enormously, and ultimately rupturing the outer layer, form a very viscous liquid which is known as starch-paste. Marked differences in the viscosity of this paste are produced by slight variations in the treatment of the starch during the processes of purification and drying. When it has been treated with potash and acid, a paste is produced of less viscosity, *ceteris paribus*, than when no such treatment has been adopted. Great variations in the consistency of the resulting paste are also produced by slightly altering the manner of drying the starch. Starch which has been dried slowly and at a low temperature always yields a more viscid solution than that which has been dried at a higher temperature. As the technical value of a starch depends to a considerable extent on its power of pro-

* Nügeli's *granulose* is evidently identical with the *amidone* of Payen & Persoz (*Ann. Chim. Phys.* lvi. 337, 1834), and with Guérin Varry's *amidine* (*Ann. Chim. Phys.* lvi. 226); the *amidin léguminaire* and *amidin soluble* of the latter author being identical with the soluble and insoluble modifications of starch-cellulose.

ducing a more or less viscid paste, these variations of viscosity may prove to be of great importance in the manufacture of starch.

The specific rotatory power of starch in a solution containing 10 grams in 100 c.c. for the transition-tint is 207.3° – 208.8° at ordinary temperatures, and is increased by boiling to 219.5° . The addition of potash to the solution diminishes the rotatory power, which, however, rises again to its original height, or sometimes a little higher, when the alkali is neutralised with acetic or carbonic acid.

Soluble Starch. Delffs in 1859 (*Pogg. Ann.* cix. 648) described a method of preparing a solution of starch by prolonged trituration of starch with sand and a quantity of cold water sufficient to convert the whole into a rather thin paste, and leaving it at rest for twenty-four hours, so that the suspended particles might settle down and not stop the filter. He found that the solution thus obtained differed in its reactions from those of dextrin, especially in giving a blue colour with iodine, and supposed that it contained a peculiar soluble modification of starch, for which he proposed the name *amylogen*. Flückiger (*Zeitschr. Ch. Pharm.* 1861, 104) prepared a similar solution by drenching starch-grains with a concentrated solution of calcium chloride, assisting the action by frequent agitation. On decanting the calcium chloride solution from the resulting gummy mass, and agitating the latter with 100 to 150 times its weight of water, a stiff jelly was obtained, and with a larger quantity of water, a clear filtrable solution which was turned blue by iodine, and exhibited all the characters of the amylogen solution described by Delffs.

According to Musculus, on the other hand (*Bull. Soc. Chim.* [2], xxii. 26; *Ann. Chim. Phys.* [5], ii. 385), the so-called amylogen is not actually soluble in water, inasmuch as its concentrated solutions stop up a filter, and the compound precipitated from it by alcohol and dried is no longer soluble in water even at the boiling heat; he supposes that the amylogen still retains the original structure of starch. Truly soluble starch, free from organised substance, is obtained by boiling ordinary starch with very dilute sulphuric acid, saturating the solution with chalk, and evaporating to a syrup. This syrup, after long standing, deposits extremely small granules which gradually increase in size; and on pouring off the syrup, washing the residue with cold water, dissolving it in hot water, and precipitating the amylogen with a little alcohol, the remaining solution yields on evaporation a perfectly white mass, which is insoluble in cold water, but dissolves readily in water at 50° , and does not separate out again on cooling. The residue left on evaporating this solution, or the precipitate obtained from it with alcohol, redissolves completely in warm water. On cooling the solution to a low temperature, the dissolved starch settles down completely as a thick sediment exhibiting the same relations of solubility. If contaminated with dextrin or glucose, it no longer exhibits its peculiar characters. It does not exert a reducing action. Its rotatory power is four times as great as that of glucose. Diastase acts upon it in the same manner as on ordinary starch, but more quickly. Its dilute solutions are coloured red by iodine, strong solutions violet. Moderately strong solutions, mixed with a quantity of iodine sufficient to give them a dark red-brown colour, assume, when evaporated in the air, a violet, and finally a blue tint, which, on dilution with water, changes again to violet and then to red. Calcium chloride throws down from the red solution a blue precipitate, apparently not identical with ordinary iodide of starch.

Bondonneau (*Compt. rend.* lxxx. 671) has prepared amylogen according to the process of Musculus, and finds that the syrup, if dried before the granular mass described by Musculus has separated out, is at first completely soluble in water, but afterwards only partially. Hence it seems probable that the body insoluble in water does not pre-exist in the starch, but is formed only in the viscid liquid. Moreover, this substance is produced only in those syrups which are turned violet by iodine, not in those which are coloured red. Amylogen prepared by the action of dilute acids or alkalis, or of water under increased pressure, is translucent after drying, and dissolves for the greater part in hot or cold water, provided it be first very finely divided, completely, however, though with various degrees of facility, in solution of sodium carbonate or zinc chloride. Amylogen prepared with sodium carbonate, and subsequent neutralisation with an acid, dissolves readily in cold water, but becomes almost insoluble therein, and very difficultly soluble in hot water, after the mass has been pressed. In the dialyser, dissolved starch behaves exactly like a colloid substance; and this circumstance affords an explanation of an experiment made by Payen, in which a filter cut out of a hyacinth-bulb was found to separate starch completely from its solution, the bulb, in fact, acting as a dialyser. The action of acids and alkalis on the starch-granule—from which, in its perfect state, water does not extract anything—depends upon their degree of concentration, and on the final rupture of the cellulose-coating, the starch in the interior being then easily dissolved.

Oxidation.—The action of various oxidising agents on soluble starch, prepared with nitric acid, has been studied by Reichardt (*Ber.* viii. 1020). Potassium permanganate in acid, neutral, or alkaline solution, also chromic acid, chlorine, and cuprous oxide, give rise to humous substances; dilute nitric acid, to carbonic and oxalic acids; bromine and silver oxide, to dextronic acid (vii. 424).

Fuming nitric acid converts soluble starch into a *mononitro-derivative*, $C_6H_5(NO_2)O_5$, which appears to differ from the corresponding compound prepared in like manner from ordinary starch by its solubility in boiling alcohol and in ether. Reichardt finds that 1 pt. of soluble starch requires for solution about 40 pts. of water at 20°.

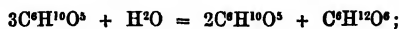
On the Fermentation of Starch under the influence of *Schizomycetes*, see FERMENTATION (p. 777).

Reactions of Starch with Iodine. A. Vogel (*N. Rep. Pharm.* xxii. 349; xxv. 565) draws attention to the fact—observed also by others—that dry starch is coloured blue by a weak alcoholic tincture of iodine, but not by a solution of iodine in absolute alcohol, or even in alcohol of sp. gr. 0.880 (66 p. c. by weight). Further, the decoloration of a solution of starch iodide by sunlight or by heat takes place more quickly in dilute than in concentrated solutions. If the heating has been continued for a short time only, the blue colour reappears on cooling; but if the heating has been prolonged, the colour is restored only on addition of nitric acid, chlorine, &c. On heating the solution, iodine escapes at first, but its evolution does not continue, and even a solution which has been completely decolorised by boiling and evaporated to dryness is still found to contain iodine. The decoloration appears to depend upon the fact that the iodine is converted into a mixture of iodic and hydriodic acids, which subsequently act upon one another in such a manner as to liberate iodine.

H. Pellet (*Monit. scient.* [3], vii. 988) regards starch iodide as a definite compound analogous in its chemical relations to the iodides of the heavy metals, mercury and silver for example, being soluble in excess of soluble starch, just as these metallic iodides are soluble in excess of potassium iodide, and reprecipitated from the solution by acids.

According to Bondonneau (*Compt. rend.* lxxxv. 671), starch iodide is a definite chemical compound represented by the formula $(C_6H^{10}O_5)_2I$. It is obtained pure when a solution of starch, prepared by the action of caustic soda on starch suspended in fifteen to twenty times its amount of water, is mixed with excess of iodine solution, then acidulated and filtered, and the resulting starch iodide is washed with water containing a little hydrochloric acid, and finally dried in the air, whereby, however, it loses a small quantity of iodine, so that its composition agrees with the formula above given only when it is moist. Starch iodide thus prepared is a hard black-violet mass, which swells up in water and then recovers its blue colour. When heated at 100° it loses 16–18 per cent. of hydriodic acid and water, and at 190° the loss amounts to 46 per cent., the colour changing to black. The black substance thus obtained yields on oxidation saccharic and oxalic acids; sulphuric acid converts it into glucose. When the iodide is heated under pressure, carbon dioxide, hydriodic acid, and iodine are evolved, and when heated to 100° with water under pressure, it partly splits up into iodine and starch, and is partly converted into glucose and hydriodic acid. Water at the ordinary temperature slowly converts it into α -dextrin and hydriodic acid. It is decomposed by diastase, yielding glucose, β - and γ -dextrin, hydriodic acid, and an organic iodide not yet separated.

Conversion of Starch into Dextrin and Sugar by the action of Diastase and of Dilute Acids. Musculus stated in 1860 that starch when boiled with dilute acid is converted into dextrin and glucose, according to the equation,



and he supposed that diastase acted upon starch in the same manner (vi. 1081). Schulze a. Märker, however (vii. 1008), found that the ferment of malt-extract does not, like sulphuric acid, convert the whole of a given quantity of starch into sugar, but only the half of it, and O'Sullivan showed (*ibid.*) that the ultimate product of the action of malt-extract upon starch is not glucose, but maltose, a substance isomeric with cane- and milk-sugar, and capable of reducing only two-thirds of the quantity of cupric salt that is reduced by dextrose.

Further experiments by Musculus a. Gruber (*Compt. rend.* lxxxvi. 1459) have led them to the conclusion that, under the influence of boiling dilute sulphuric acid, or of diastase, the following substances are produced from starch.

1. *Soluble Starch.*—Insoluble in water at 50°–60°. Coloured wine-red by iodine in aqueous solution, and blue in the solid state. Dried in the air with excess of

iodine, it assumes violet, yellow, or brown tints. Rotatory power $[\alpha]_D^{20} = +218^\circ$, reducing power 6.

2. *Erythrodestrin*, which constitutes half of the dextrin of commerce, always strikes a red colour with iodine, whether it be solid or in solution. It is never insoluble in water. Very easily attacked by diastase.

3. *Achroodestrin*, α . Not coloured by iodine. Rotatory power $[\alpha]_D^{20} = +210^\circ$; reducing power, 12. Partially convertible into sugar by diastase, but less easily than soluble starch or erythrodestrin.

4. *Achroodestrin* β . Not attacked by diastase, at least during the first twenty-four hours. Rotatory power $[\alpha]_D^{20} = +190^\circ$; reducing power, 12.

5. *Achroodestrin* γ . Not attacked by diastase at all; changed into glucose by boiling with dilute sulphuric acid for several hours. Rotatory power $[\alpha]_D^{20} = +150^\circ$; reducing power, 28.

6. *Maltose*, $(C^{12}H^{22}O^{11} + H^2O)$.—Attacked with difficulty by diastase; fermentable. Rotatory power $[\alpha]_D^{20} = +150^\circ$; reducing power, 66.

7. *Glucose*, $(C^6H^{12}O^6 + H^2O)$.—Fermentable. Rotatory power $[\alpha]_D^{20} = +56^\circ$; reducing power, 100.

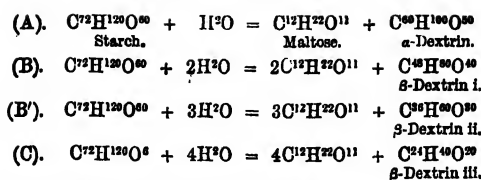
Musculus a. Gruber regard starch as a polysaccharide of the formula $n(C^{12}H^{22}O^{10})$, in which the exact value of n , apparently not less than 5 or 6, remains to be determined. Under the influence of diastatic ferments and of dilute acids, this carbohydrate takes up water by successive stages, and breaks up into maltose and a new dextrin of successively smaller molecular weight, n becoming less at each stage, until the transformation has gone as far as the production of achroodestrin γ , which is probably transformed into maltose by simple hydration, the maltose then in its turn taking up water and splitting up in the manner shown by the equation: $C^{12}H^{22}O^{11} + H^2O = 2C^6H^{12}O^6$.

In the action of diastase on starch a large quantity of maltose is produced, together with only a small quantity of dextrose, whereas when sulphuric acid is used, dextrose is produced in considerable quantity.

M. A. Petit (*Bull. Soc. Chim.* [2], xxiv. 519) finds that when starch is subjected for several hours to the action of diastase at 50° , and the liquid is subsequently boiled, the starch is almost wholly converted into sugar, so that alcohol throws down from the solution only 5 per cent. of dextrin. The sugar solution was found to contain, besides maltose, a fermentable sugar which did not reduce Fehling's solution, even after boiling for five minutes with dilute sulphuric acid. The quantity of this sugar amounted to about three-fourths of the maltose obtained. When treated with yeast, it gave off a quantity of carbon dioxide equal to that which would have been evolved from the same quantity of glucose.

According to Herzfeld (*Ber.* xii. 2120), the final products of the action of diastase on starch are maltose and achroodestrin. At temperatures above 65° , another body appears also to be produced in the form of a slightly-coloured uncrystallisable gummy mass, very soluble in water, having a faint sweet taste, due perhaps to its partial conversion into sugar. It has about one-third the reducing power of maltose. This body, which Herzfeld calls *maltodextrin*, is identical with Bondonneau's γ -dextrin. Its acetyl-compound differs from those of erythro- and achroodestrin in not separating out from its solution in hot alcohol, even when considerable quantities of it are dissolved.

From later experiments by O'Sullivan (*Chem. Soc. J.* 1876, xxx. 125), it appears also that the only products of the action of diastase on starch are dextrin and maltose; further, that malt-extract prepared without the aid of heat does not alter ungelatinised starch, but acts upon starch only at the temperature of gelatinisation, which is different for the several varieties of starch, and even for starch-granules of different sizes: for potato-starch it is 63° – 64° . On starch-paste diastase acts even at 10° – 20° , producing maltose and dextrin in the ratio of 67 : 32 per cent., which, however, by prolonged action and further addition of malt-extract, is raised to 82 : 18. If the solution is formed at 63° , and cooled after a few minutes, the quantities of maltose and dextrin obtained are constantly 67.85 and 32.15, agreeing nearly with equation A (below). If the temperature of the reaction lies between 64° and 68° – 70° , the quantities of the two products are 34.54 and 65.46 per cent. (equation B.); at 68° – 70° they are 17.4 and 82.6 (equation C.); and under other circumstances (not specified) proportions of maltose and dextrin have been observed agreeing with equation B'.



The optical rotatory powers and cupric reducing powers of these dextrans are as follows:—

	Optical rotatory power	Reducing power
α -Dextrin	218·8° and 219·5°	0·14 to 0·018
β -Dextrin i.	210°	12
β -Dextrin ii.	216°–217·5°	3·0 to 3·6
β -Dextrin iii.	216°–217°	2·5 to 0·6

From a study of the action of malt-extract on these transformation-products, O'Sullivan infers that the theory advanced by Musculus a. Gruber of the breaking down of the starch-molecule into dextrin-molecules which become smaller and smaller at every step, is not in accordance with all the facts observed; and he regards these bodies, not as a series of polymerides, but rather as a series of bodies of the same molecular weight, in which the differences of behaviour must be accounted for by differences in the arrangement of the molecules, probably in solution only. It may be supposed that the molecule of soluble starch, or the dextrin which gives a purple colour with iodine, is simply $\text{C}^{12}\text{H}^{20}\text{O}^{10}$; but that these molecules in solution are arranged in groups of six sizes, all the groups being in an intimate state of tension one with another, so that the motion affecting one under certain conditions, likewise affects all under the same condition.

* Brown a. Heron (*Chem. Soc. J.* xxiv, 620–654), from a study of the transformation of soluble starch by malt-extract, conclude that the most probable formula of soluble starch is $10\text{C}^{12}\text{H}^{20}\text{O}^{10}$. The first action of the transforming agent of malt-extract is the hydration of one of the ten groups $\text{C}^{12}\text{H}^{20}\text{O}^{10}$, and the consequent production of maltose, $\text{C}^{12}\text{H}^{22}\text{O}^{11}$, the other nine groups forming erythrodextrin α . This dextrin on further hydration splits up into a molecule of maltose and erythrodextrin β , consisting of eight groups $\text{C}^{12}\text{H}^{20}\text{O}^{10}$; and this last in its turn splits up into a dextrin formed of seven such groups, which is the first achroodextrin. In this way the degradation of the original molecule proceeds, until by successive stages of hydration maltose is reached.

The number of distinct dextrans which, according to this hypothesis, are possible depends upon the molecular weight of the lowest possible dextrin. If a dextrin is capable of existing containing the same number of carbon-atoms in its molecule as maltose, nine distinct stages in the transformation may be expected; whereas, if the lowest dextrin contains double as many carbon-atoms as maltose, there can only be eight.

The following table represents the values of the specific rotatory power $[\alpha]_{\text{D}^{386}}$, and cupric reducing power, $\text{K}_{\text{D}^{386}}$, for the joint products of each of these theoretical transformations, the resulting dextrans being enumerated in the last column.

No. of transformation	$[\alpha]_{\text{D}^{386}}$	$\text{K}_{\text{D}^{386}}$	Resulting dextrin
Soluble starch	216·0°	0	—
(1)	209·0	6·4	Erythrodextrin α
(2)	202·2	12·7	" β
(3)	195·4	18·9	Achroodextrin α
(4)	188·7	25·2	" β
(5)	182·1	31·3	" γ
(6)	175·6	37·3	" δ
(7)	169·0	43·3	" ϵ
(8)	162·6	49·3	" ζ
(9)	156·3	55·1	" η
Maltose	150·0	61·0	—

Of these possible transformations the experiments of Brown a. Heron have unmistakably established the existence of Nos. (2), (3), (4), and (8), whilst indications of (5) and (6) have frequently been obtained in various ways, but not with the same amount of certainty as in the other cases.

* The number 3·86 is the divisor required to convert the specific gravity of the solution into grams of dry substance in 100 c.c., or the value of x in the equation $x=10\left(1-\frac{1}{y}\right)$ where y is the specific gravity.

The dextrins corresponding to Nos. (1) and (2) are erythrodextrins; all the others are achroodextrins.

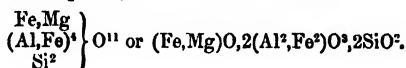
R. Sachsse (*Chem. Centr.* 1877, 732) infers, from the quantity of sugar obtained by treating starch with hydrochloric acid, that the molecular formula of dry starch is $C^{36}H^{62}O^{31}$. Starch in its ordinary state he regards as a hydrate, $C^{36}H^{62}O^{31} + 12H^2O$, inasmuch as potato-starch in drying sustains a loss of weight amounting to 17·7 per cent., the formula just given requiring 17·5 per cent. This view is supported by the observation that when dry starch is brought in contact with a small quantity of water, a rise of temperature is produced amounting to 15° – 40° or upwards. Perhaps the constitution of dried starch might be represented by the formula $C^{36}H^{60}O^{30} \cdot H^2O$, and that of the hydrate by $C^{36}H^{60}O^{30} \cdot H^2O + 12Aq$, 1 mol. of the water being basic, and the rest less intimately combined, like water of crystallisation; or these formulæ might be doubled to accord with the results obtained by Brown & Heron.

Tollens, by precipitating an alkaline solution of gelatinous starch with alcohol and ether, has obtained compounds containing 4 or 5 at. $C^6H^{10}O^5$ to 1 at. K or Na, whence he infers that the molecule of starch must contain 24 or 30 atoms of carbon.

Estimation of Starch. On the Estimation of Starch by Bloch's Feculometer, see Cloëz (*Dingl. pol. J.* cxxi. 397; *Zeitschr. anal. Chem.* 1874, 337); also Bondonneau (*Bull. Soc. Chim.* [2], xxi. 147; *Zeitschr. anal. Chem.* 1874, 467). On the amount of Starch in Potatoes, see POTATOES (p. 1669); also Siewert (*Landw. Versuchs.-St.* xxiv. 427; *Chem. Soc. J.* xxxviii. 512); Behrend, Maercker & Morgen (*Landw. Vers.-St.* xxv. 107–165; *Chem. Soc. J.* xxxviii. 513); in Sausages (Medicus & Swale, *Ber.* xii. 1285; *Chem. Soc. J.* xxxvi. 939).

Manufacture. The present state of the Starch-manufacture is described by C. Scheibler in Hofmann's *Entwicklung der chemischen Industrie*, iii. 152; that of the Rice-starch Manufacture by M. Adlung (*Dingl. pol. J.* cxxi. 58, 543; *Chem. Soc. J.* xxx. 675; xxxi. 363); the manufacture of Wheat-starch in Halle, by Adlung (*Dingl.* cxxiv. 304; *Jahresb. f. Chem.* 1877, 1207).

STAUROLITE. According A. v. Lasaulx (*Min. Mitth.* 1872, 173), most staurolites contain a considerable number of microscopic enclosures (chiefly quartz, with garnet, mica, magnetic iron oxide, and brookite), and to these he attributes the variations in the analytical values, especially that of the silica (v. 412). From an analysis of staurolite from Monte Campiano, near Faido, which microscopical examination showed to be the purest, he deduces the formula:



The analysis gave:

SiO^2	Al^2O^3	Fe^2O^3	FeO	MgO	H^2O	Sp. gr.
29·81	48·26	5·31	12·03	3·25	0·86 = 99·52	3·71

Rammelsberg finds (*Ber.* vi. 127) that when staurolites rich in enclosed silica are treated with hydrofluoric acid, the free silica is dissolved, and a residue is left agreeing in composition with pure staurolite from the St. Gothard. In staurolites which contain only a small quantity of free silica, the hydrofluoric acid partly decomposes the silicate, but in this case also a summation of the constituents of the decomposed and undecomposed portions leads to the same composition (No. 5):

	TiO^2	SiO^2	Al^2O^3	FeO	MgO	H^2O	
1.	0·56	29·46	52·29	13·42	2·29	1·42 =	99·44
2.	30·24		52·59	13·86	2·81	1·60 =	101·10
3.	0·16	30·23	52·85	14·65	2·41	—	—
4.	0·39	30·23	51·16	14·66	2·73	1·26	—
5.	1·00	31·76	50·03	14·18	2·07	0·96	—

1 and 2. Gothard. 3. Pitkaranda; the residue left after treatment with hydrofluoric acid amounts to 61 per cent. The acid dissolved out—together with 35·2 per cent. SiO^2 —only 1·3 Al^2O^3 , 2·4 FeO , and 0·1 MgO . 4. Bretagne; original amount of silica 50·75 per cent. 5. Bretagne.

Staurolite from the Culsagee mine, where it occurs in small blue grains of sp. gr. 3·711, interstratified with damourite, has been analysed by F. A. Genth (*J. pr. Chem.* [2], ix. 49) with the following results:

SiO^2	Al^2O^3	Fe^2O^3	FeO	MgO	CaO	Loss by ignition
27·91	52·92	6·87	7·80	3·28	trace	1·59 = 100·37

STEARIC ACID, $C^{18}H^{36}O^2$. Occurrence.—Stearin, the glyceride of this acid

occurs, together with palmitin and olein, in the fat of parsley seeds (E. v. Gerichten, *Ber.* ix. 1126).

Formation from Ricinoleic acid.—When phosphorus and iodine are gradually added to a warm emulsion of ricinoleic acid with a small quantity of water, a yellow oil is formed, consisting of *iodostearidenic acid*, $C^{18}H^{33}IO_2$, and this acid, treated with nascent hydrogen (zinc-foil and dilute hydrochloric acid), is converted into stearic acid. *Iodo-stearidenic acid* easily takes up 2 at. bromine, forming the acid $C^{18}H^{33}BrIO_2$ (Claus a. Hassenkamp, *Ber.* ix. 1916).

Decomposition by Heat.—Stearic acid may be distilled under ordinary atmospheric pressure, almost without decomposition, but when distilled four times or more in a closed vessel, it is almost wholly resolved into hydrocarbons, water, and carbon dioxide, together with small quantities of acids and ketones. The liquid portion of the product thus obtained was found to contain, besides water ($\frac{1}{3}$ of the whole weight), all the members of the paraffin series from C^6 to C^{15} , and all those of the olefine series from C^3 to C^{15} . Lower members of both series were contained in the resulting gases (G. Johnston, *Chem. Soc. J.* xxix. 8).

On the Manufacture of Stearic acid, see Ramdohr (*Dingl. pol. J.* cccix. 518; *Jahresb. f. Chem.* 1876, 1092).

On the separation of Stearic from Oleic acid in mixtures produced by the saponification of Fats, see OLEIC ACID (p. 1432).

STEARIC ACID, $C^{18}H^{36}O_2$. This acid, discovered by Overbeck (vi. 1038), is converted, by oxidation with fuming nitric acid, into a greenish oil coagulating to a semi-solid mass from which water extracts azelaic acid, $C^{10}H^{18}O_4$. The alcoholic solution of the residue deposits stearoxylic acid, $C^{18}H^{32}O_4$, in greenish laminae; and the mother-liquor separates into two layers, viz. an alcoholic liquid containing only a small quantity of stearoxylic acid, and an oily layer, which does not contain azelaic aldehyde, $C^8H^{16}O_2$, as stated by Overbeck, but, on saponification, yields pelargonic acid, $C^9H^{18}O_2$, together with nitrosopelargonic acid, $C^9H^{16}(NO)^2O_2$ (vi. 503), which detonates when heated. Ethyl pelargonate, $C^9H^{17}O_2.C^2H_5$, is also formed in this reaction (L. Limpach, *Liebig's Annalen*, xc. 294).

STEPHANUS SEEDS, ALKALOIDS OF. The alkaloids of the seeds of *Delphinium Staphisagria* have been examined by Marquis (*Russ. Zeitschr. Pharm.* xvi. 449, 481, 513). The bruised seeds (1–2 kg.) were repeatedly exhausted with four times their weight of alcohol of 90 per cent. containing 5 to 10 grams of tartaric acid; the resulting alcoholic solution was distilled in a vacuum; the residue, which contained a green oily layer, was separated from the latter in a tap-funnel, then immediately mixed with acid sodium carbonate in quantity sufficient to give it a slight alkaline reaction, and agitated with ether. The ethereal solution thus obtained left on spontaneous evaporation crystals of delphinine; the mother-liquor contained delphinoidine or delphisine; and the liquid exhausted with ether yielded to chloroform the amorphous base, staphisagrine. The oil, which holds in solution a considerable quantity of alkaloids, is shaken with water very slightly acidulated with sulphuric acid to separate these bases, and the resulting solution is treated as above. In favourable cases, 2·5 kg. of seeds thus treated yield 18·1 grams of alkaloids soluble in ether, and 10·59 grams of crude staphisagrine, altogether 1·15 per cent. of alkaloids.

The *delphinine* crystallised from ether is purified by treatment with the same solvent; the uncrystallisable mother-liquors are evaporated down; the residue is dissolved in water containing tartaric acid to separate resinous decomposition-products of *delphinoidine*, then immediately saturated with acid sodium carbonate, and again digested with ether; and the residue insoluble therein is dissolved in a small quantity of pure chloroform and then mixed with a four- or five-fold quantity of ether, whereupon *staphisagrine* separates out, and *delphinoidine* is left on evaporation. This last base, when pure, is colourless, completely soluble in acidulated water, and dissolves in ether free from alcohol, yielding a solution which is not rendered turbid by excess of the solvent. To purify the staphisagrino, the contrary method is adopted; that is to say, it is repeatedly precipitated by ether from solution in chloroform; it has not been obtained colourless.

Delphinine, $C^{22}H^{35}NO^6$ (at 100°). This base crystallises in the orthorhombic system, with the axial ratio $a : b : c = 0·63736 : 1 : 0·80402$. Most frequent combination P. OP. ∞ P. ∞ . It decomposes at 120° without fusion. At 20° it dissolves in 5000 pts. water, 20·8 alcohol of 98 per cent., 11·1 ether, and 15·8 chloroform. Its alcoholic solution is optically inactive, and exhibits only a slight alkaline reaction. It tastes, at first, purely bitter, but afterwards produces a cooling and benumbing sensation. It dissolves in pure sulphuric acid, with faint brownish colour, changing to reddish and violet, but does not produce any other conspicuous colour-reactions. The *aurochloride* has the composition $C^{22}H^{35}NO^6.HCl.AuCl^3$; the *mercuriodide*,

$C^{22}H^{33}NO^6, HI, HgI^2$. From gravimetric saturation-experiments, the composition of the *sulphate* appears to be $3C^{22}H^{33}NO^6, H^2SO^4$; that of the *nitrate*, $3C^{22}H^{33}NO^6, 2HNO^3$; of the *hydrochloride*, $3C^{22}H^{33}NO^6, 2HCl$, but volumetric determinations gave different formulæ for the sulphate and nitrate.

Delphinoidine, $C^{42}H^{68}N^2O^7$ (?) This base dissolves in alcohol in all proportions, in water in the proportion of 1 : 6475, in absolute ether 1 : 3, and still more abundantly in alcoholic ether; easily also in chloroform. In alcoholic solution it has an alkaline reaction, a bitter taste, with after-taste like that of delphinine, and is optically inactive. It melts between 110° and 120° (?). Its colour-reactions are those which were formerly ascribed to delphinine. Sulphuric acid dissolves it with dark brown colour changing to red-brown. With sugar and sulphuric acid it becomes first brown, then green; with sulphuric acid and bromine-water it produces a splendid violet colour. It decomposes during drying. Its *platinochloride*, like that of delphinine, is very soluble in water, and extremely unstable. The *aurochloride* has the composition $C^{42}H^{68}N^2O^7, 3HCl, 2AuCl^3$. Saturation-experiments gave for the *sulphate* the formula $C^{42}H^{68}N^2O^7, H^2SO^4$; for the *nitrate*, $C^{42}H^{68}N^2O^7, 2HNO^3$; for the *hydrochloride*, $C^{42}H^{68}N^2O^7, 2HCl$, and for the *acetate*, $C^{42}H^{68}N^2O^7, 2C^2H^4O^2$.

Delphisine, $C^{27}H^{46}N^2O^4$ (?) This alkaloïd, in one instance, when fresh seeds had been used, crystallised from the mother-liquors of delphinine. It resembles delphinoidine in its colour-reactions, and is not much less soluble than the latter in alcohol and in chloroform, but contains a much larger proportion of nitrogen.

Staphisagrine, $C^{22}H^{33}NO^5$, is always amorphous, dissolves in 200 pts. of water, and 855 pts. of ether, and in all proportions of alcohol and chloroform; tastes like delphinine; melts at a temperature somewhat above 90° . In alcoholic solution it is optically inactive, and has an alkaline reaction. It differs from delphinoidine in its colour-reactions, being coloured by sulphuric acid cherry-red to violet, less strongly the purer it is—by sugar and sulphuric acid only dirty brown—and by sulphuric acid and bromine only faintly and transiently reddish. Nitric acid colours it red to brown. Its *aurochloride* has the composition $C^{22}H^{33}NO^5, HCl, AuCl^3$; the *mercuriodide* $C^{22}H^{33}NO^5, HgI^2$ (?) Its other salts, analysed as above, appear to be composed as follows: *sulphate*, $(C^{22}H^{33}NO^5)_2H^2SO^4$; *nitrate*, $C^{22}H^{33}NO^5, HNO^3$; *hydrochloride*, $C^{22}H^{33}NO^5, HCl$; *acetate*, $C^{22}H^{33}NO^5, C^2H^4O^2$.

STERNBERGITE. See SILVER SULPHIDES.

STERLINGITE. See VERMICULITES.

STILBENE ALCOHOLS, $C^{14}H^{14}O^2 = C^{14}H^{12}(OH)^2$. *Hydrobenzoin*s.—The experiments of Forst a. Zincke and of Zincke a. Breuer on these alcohols have already been described in this volume under DIPHENYLENE ALCOHOLS (p. 679). The following additional results have been obtained by Breuer (*Inaugural dissertation*, Marburg, 1877).

The two solid products (*anhydrides*) obtained from hydrobenzoin and isohydrobenzoin by the action of dilute sulphuric acid, have the composition $(C^6H^5CH)^2O$, and boil at 131° and 100° respectively. They are but slightly acted upon by benzoic and acetic anhydrides; but hydrobenzoin-anhydride heated with benzoic acid for seventeen hours at 230° – 240° , yields the corresponding benzoic ether melting at 240° – 243° ; and with acetic acid at 160° – 170° the acetic ether which melts at 134° . The reaction with benzoic acid also yields stilbene. Isohydrobenzoin-anhydride reacts differently with benzoic and acetic acid, yielding stilbene, together with bitter almond oil (recognisable by its odour), but only very small quantities of ethereal products. With

benzoyl chloride, both these anhydrides yield stilbene chloride, $(C^6H^5)^2 \begin{matrix} \diagup CHCl \\ | \\ \diagdown CHCl \end{matrix}$, melt-

ing at 192° . *Phosphorus pentachloride*, heated with hydrobenzoin-anhydride for half an hour at 130° , yields chiefly stilbene chloride; with isobenzoin-anhydride it yields first a chloride, convertible by acetic acid and silver acetate into hydrobenzoin, while stilbene chloride is produced only at a later stage of the reaction. Both the anhydrides, when heated for eight hours at 200° with hydriodic acid and phosphorus, are converted into dibenzyl (m. p. 51° – 52°). Both, when treated with chromic and glacial acetic acid, yield, as chief product (together with benzoic acid), a body having the composition $C^{22}H^{22}O^2$, which dissolves sparingly in hot alcohol, and crystallises therefrom in small felted needles melting at 155° , easily soluble in benzene, slightly in petroleum-ether. This body, heated for 12 hours in a sealed tube at 200° with hydriodic acid and amorphous phosphorus (1 gram of substance, 0.5 phosphorus, and 2.5 hydriodic acid), yields, together with dibenzyl, a substance melting at 144° – 145° , and separable from the dibenzyl by distillation with steam, in which it does not volatilise. This last substance appears to have the composition $C^{14}H^{12}O^2$, and to be formed as a third oxidation-product of the anhydrides.

The liquid product, *diphenylacetaldehyde*, $(C^6H^5)_2CH-CO^H$, obtained from hydrobenzoin and isohydrobenzoin by the action of dilute sulphuric acid (p. 681), boils at 315° , and gradually decomposes on keeping. It dissolves in acid potassium sulphate, forming a crystalline compound which, however, is very unstable, and has not been obtained pure. It reduces an ammoniacal silver solution, and is converted by oxidation with moist silver oxide, potassium permanganate, and chromic acid, into benzophenone, benzoic acid being also produced when permanganate is employed as the oxidiser. With alcoholic potash at $120^\circ-130^\circ$, the aldehyde yields benzhydrol, together with diphenylmethane and diphenylacetic acid.

The above-described anhydrides and aldehyde are also produced by heating the hydrobenzoins in alcoholic solution with zinc chloride and hydrochloric acid at $130^\circ-150^\circ$ (Breuer).

Stilbene Sulphide, $C^{14}H^{12}S$, also called *Sulphostilbene*, separates, according to Barbier (*Ann. Chim. Phys.* [5], vii. 522), from the products of the dry distillation of benzyl sulphide, $(C^7H^7)_2S$, which have been used for the preparation of stilbene (p. 676). It forms light white needles melting at $168^\circ-169^\circ$, unites with picric acid, forming red opaque needles, and with Fritzsche's reagent, forming light yellow rhombic lamellae. According to Forst, the sulphur-compound obtained as above is not stilbene sulphide, but probably impure tolyl-allyl sulphide, $(C^6H^5.C)^2S$.

STILSITE. See ZEOLITES.

STORAX. The constituents of liquid storax have been investigated by W. v. Miller (*N. Rep. Pharm.* xxiv. 1; *Ber.* ix. 274; more fully, *Liebig's Annalen*, clxxxviii. 184; clxxxix. 338). This substance contains, in addition to the previously known constituents, styrolene, cinnamic acid, and styracin (i. 497, 986), the following bodies: (1). Phenyl-propyl cinnamate in somewhat considerable quantity; (2). Ethyl cinnamate in small quantity; (3). A crystallisable substance combining with acid sodium sulphate, smelling like vanillin, and melting at 65° (ethyl-vanillin?) in very small quantity; (4). A resinous body, whose composition could not be determined, accompanying the last in moderately large quantity; (5). Two alcoholic bodies (α - and β -storesinol) in very considerable quantity; (6). The cinnamic ethers of these alcohols in not inconsiderable quantity; (7). The sodium-derivative of storesinol in very small quantity.

Styrolene from liquid storax, and cinnamene from cinnamic acid, are regarded by v. Miller as identical; van't Hoff's *styrocamphe* (*Bull. Soc. Chim.* [2], xxv. 175), described as a laevogyrate substance having the composition $C^{10}H^{18}O$ or $C^{10}H^{16}O$, is perhaps not an original constituent of storax, but is formed subsequently by decomposition of phenylpropyl cinnamate.

Testing of Liquid Storax.—To detect the presence of turpentine, H. Hager (*Zeitschr. anal. Chem.* 1874, 247) mixes the liquid storax in a test-glass with half its volume of absolute alcohol, and agitates the mixture repeatedly with several times its volume of petroleum-ether. If the storax is pure, the residue left on evaporating this solvent is colourless with a bluish opalescence, and has a pleasant odour, but in presence of turpentine it is yellowish, and has an unmistakable odour of that substance. With good liquid storax the residue amounts to about 50 per cent.; if it exceeds this proportion, the presence of adulteration may be suspected.

STORESINOL, $C^{36}H^{58}O^3 = C^{36}H^{53}(OH)^3$, is the residue left after exhausting liquid storax successively with caustic soda, cold alcohol, cold petroleum-ether, and hot petroleum-ether. It melts between 160° and 168° , and is oxidised in glacial acetic acid solution by chromic acid, with evolution of carbon dioxide and formation of three acids not yet examined. With acetyl chloride it yields a mono- and a tri-acetyl derivative. Bromine converts it into a bromide having the composition $C^{36}H^{53}Br^3$.

STRENGITE. This mineral occurs in an isolated ironstone and psilomelane-block in the siliceous slate of the great brown iron-ore deposit of Dünsberg, near Giessen, in globular, reniform, and radio-fibrous aggregations, having a drusy surface and often accompanied by very fine cacoene. Rarely isolated crystals are found, possessing a strong vitreous lustre. These crystals are transparent or translucent, red in various shades (pomegranate-red and carmine-red), also white, and occasionally colourless; streak yellowish-white; hardness 3-4; sp. gr. 2.87. Before the blowpipe the mineral fuses easily to a black, shining globule, colours the flame bluish-green, and gives the reactions for iron. On heating it in the matrass, much water is evolved, whilst hydrochloric acid dissolves it easily, especially when hot, but it is not easily attacked by nitric acid. In order to obtain pure material for analysis, selected portions

of the mineral were treated with stannous chloride solution, which dissolved out the brown iron-ore and left the small isolated crystals of strengite behind. An analysis of these showed the mineral to have the following composition :

Fe ² O ³	P ² O ⁵	H ² O
43.18	37.42	19.40 = 100.00

from which the formula $\text{Fe}^2\text{O}^3\text{P}^2\text{O}^5 + 4\text{H}^2\text{O}$ is obtained. Strengite belongs therefore to the same class of minerals as scorodite, $(\text{Fe}^2\text{O}^3\text{As}^2\text{O}^5 + 4\text{H}^2\text{O})$, and the barrandite of von Zepharovich, $\left\{\frac{2}{3}\text{Fe}^2\text{O}^3\right\}\text{P}^2\text{O}^5 + 4\text{H}^2\text{O}$; it crystallises in the rhombic system, the forms observed in combination being $\infty \bar{P} \infty . \infty \bar{P} 2 . P . m \bar{P} \infty$; the latter could not be accurately determined. Cleavage indistinct, parallel to $\infty \bar{P} \infty$, a pearly, vitreous lustre characterising the cleavage-planes. The habit of isolated crystals is 'thin-tabular' through $\infty \bar{P} \infty$, but the commonest occurrence is a sheaf-like aggregation on which only the faces of P are visible. Numerous measurements of the crystals were made, with the following results :

Angle of the terminal edge of P in the macrodiagonal	= 102° 14'
" " " " " brachydiagonal	= 115° 8'
Angle of the prism " " " " "	= 118° 36'

Mean ratio of the lengths of the axes obtained from the above measurements, $a : b : c = 1 : 1.1855 : 1.1224$, whence are calculated the angles as follows, viz. :

Macrodiagonal terminal edge of P	= 101° 38'
Brachydiagonal " "	= 115° 36'
Lateral edge of P " " "	= 111° 30'

These calculated angles agree very closely with the measurements obtained with scorodite by Breithaupt, Miller, von Zepharovich, von Kokscharow, and vom Rath, viz. :

Macrodiagonal terminal edge of P	= 102° 28'
Brachydiagonal " "	= 114° 28'
Lateral edge of P " " "	= 111° 42'

It appears, therefore, that strengite and scorodite are isomorphous. Their resemblance in form and occurrence is very striking, and their complete isomorphism may be regarded as a further proof of the close analogy of arsenic acid and phosphoric acid to each other. They are probably the final members of the series of phosphatic minerals to which pyromorphite and mimetosite belong (A. Nies, *Jahrb. f. Min.* 1877, 8).

STRIGOVITE. This mineral occurs at Striegau in Silesia. An analysis by Websky (*Jahrb. f. Min.* 1874, 302) of a specimen from a recently opened druse gave :

SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO	H ² O
28.425	16.604	11.432	26.211	7.247	0.364	0.364	9.309 = 99.956

Neglecting the slight excess of water over 2 mols., the empirical constitution of strigovite dried at 100° is $\text{H}^1(\text{M}^{\text{II}})^2(\text{R}^2)^4\text{Si}^2\text{O}^{11}$, in which $(\text{M}^{\text{II}})^2 = \frac{2}{3}\text{Fe} + \frac{1}{3}(\text{Mn}, \text{Ca}, \text{Mg})$, and $(\text{R}^2)^4 = \frac{2}{3}\text{Al} + \frac{1}{3}\text{Fe}$. Among species nearly allied to strigovite, Websky enumerates aphrosiderite from Weillburg; dolessite from La Grève, near Melin; cronstedtite from Příbram; thuringite from Reichmannsdorf and Schmiedefeld, and owenite from the Potomac river.

STROMEYERITE. A silver-copper glance, forming the principal ore of a mine on the Hoya, in the north of the province of Catamarca, Argentine Republic. It occurs, partly with small quantities of copper pyrites and galena, intergrown in tile-ore, partly in the interior of nodules consisting externally of chrysocolla with a small quantity of cerusite. An analysis by Siewert gave :

Ag	Cu	S	Insol.	Sp. gr.
52.60	31.61	14.38	1.07 = 99.66	6.15-6.19

(A. Stelzner, *Min. Mitth.* 1873, 250).

STRONTIANITE. H. Laspeyres describes crystals of strontianite (strontium carbonate) from Hamm, in Westphalia, which, contrary to the usual acuminated forms of this mineral, exhibit obtuse pyramids and brachydromes (*Jahrb. f. Min.* 1876, 431). According to F. Hessenberg (*ibid.* 1870, 626), nineteen forms are observed on strontianite, whereas on the isomorphous mineral, aragonite, only fifteen can be recognised. Sandberger (*ibid.* 589) describes strontianite as the petrifying material of an ammonite from the liroconite of Wasseraalfingen.

STRONTIUM. This element has been detected in the sun's atmosphere by

C. A. Young (*Sill. Am. J.* [3], iv. 356). It exists, together with barium, in all primary rocks, in sufficient quantity to be easily determined in a single gram of felspar, mica, gneiss, granite, or syenite (Dieulafait, *Ann. Chim. Phys.* [5], xv. 530; *Chem. Soc. J.* xxxvi. 444). Sea-water also contains strontium, both as carbonate and as sulphate, and when it is evaporated, either spontaneously or with the aid of heat, the strontium carbonate is precipitated, together with the calcium carbonate and sulphate, whilst the deposits of sodium chloride and those from the mother-liquors are free from it. From the sea-water it passes and has passed into the shells of conchylia, recent and fossil, which, as well as the gypsums of various formations, all contain strontium. Strontium has also been detected in certain mineral springs, and may be assumed to exist in all, since, according to Dieulafait, these springs derive their saline constituents chiefly, and in most cases exclusively, from the sedimentary rocks, all of which, being deposits from ancient seas, contain strontium (*Compt. rend.* lxxxiv. 1303).

Preparation and Properties of the Metal.—Benno Franz (*J. pr. Chem.* cvii. 253) has prepared strontium in considerable quantities by heating an amalgam of the metal in an iron crucible through which a stream of well-dried hydrogen is passed. The strontium then remains in the form of a fused cake, easily removable from the crucible. The strontium-amalgam is prepared by heating a saturated solution of strontium chloride with sodium-amalgam at 90° , repeating this treatment several times, then washing the resulting strontium-amalgam well with water, and drying it thoroughly between bibulous paper.

Strontium prepared as above is a faintly yellowish metal which resembles barium, and may with moderate facility be beaten out into thin laminae. In contact with the air it oxidises rapidly, with great evolution of heat, and burns away with omission of sparks. It melts at a moderate red heat, but does not volatilise even at a bright red heat. Sp. gr. = 2.4.

Estimation and Separation.—On the estimation of strontium as sulphate, see P. Schweitzer (*Proceedings of the American Association for the Advancement of Science*, 1877). Strontium sulphate dissolves on the average in 8,000 pts. of cold water; but the solubility varies, according to circumstances, from 7,500 to 10,288 pts. water.

On the separation of Strontium from Barium as Chromate, see BARIUM (p. 142).

Oxides.—Strontia, SrO (also lime and baryta), may be obtained in crystals belonging to the regular system by heating the nitrate (15 to 20 grams) in a covered porcelain crucible placed in a coke fire. The crystals thus obtained cleave parallel to the cubic faces, and the best specimens are perfectly transparent. The specific gravities and specific volumes of the three crystallised oxides are as follows:

	CaO	SrO	BaO
Specific gravity	3.251	4.750	5.722
Specific volume	17.225	21.789	26.739

The values for strontia are very nearly the means between those for lime and baryta (Brügelmann, *Wiedemann's Annalen*, iv. 277).

Hydroxide, SrH^2O^2 .—On the Heat of Formation of this Compound, see p. 959; on the Heat of Formation of the Hydrate, $\text{SrH}^2\text{O}^2 + 9\text{H}^2\text{O}$, see p. 982; on its Heat of Solution, p. 1001.

The dry hydroxide is not attacked by chlorine, but the hydrates with 5 and 8 mols. water of crystallisation are converted by chlorine into chlorate and chloride of strontium, together with a small quantity of hypochlorite (König, Weisberg, *Ber.* xii. 511).

The **peroxide**, SrO^2 , is formed when strontium carbonate is heated in a platinum crucible only so far as to make the bottom of the crucible red-hot; at a higher temperature it is decomposed. The carbonates of calcium and barium are converted by similar treatment into peroxides, that of barium having a yellow colour (H. Struve, *Zeitschr. anal. Chem.* 1872, 22).

On the Industrial Uses of Strontium-Compounds, see Biedermann (*Hofmann's Entwicklung der chemischen Industrie*, ii. 514).

STROPHANTIN. A poisonous substance extracted from the seeds of *Strophantus hispidus*, which are used in Africa as an ordeal. It forms colourless crystals, soluble with neutral reaction in water and alcohol, and not exhibiting the properties either of an alkaloid or of a glucoside. The seeds also contain a non-poisonous alkaloid called *ineine* (Hardy a. Gallois, *Compt. rend.* lxxxiv. 261). See also T. R. Fraser (*Arch. Pharm.* [3], iii. 229).

STRUVITE. Native ammonio-magnesium phosphate, $(\text{NH}^4)\text{Mg}^2\text{P}^2\text{O}^8, 12\text{aq.}$

(iv. 570). The occurrence of this mineral in an old dung-pit at Brunswick is noticed by E. J. Ottmer (*Jahrb. f. Min.* 1873, 400) and by R. Otto (*Ber.* 1873, 783). According to A. Sadebeck (*Min. Mitth.* 1877, 950), the axial ratio $a:b:c = 0.5567 : 1 : 0.9121$. The cleavage according to OP is more distinct than that according to the brachydiagonal, which has hitherto been regarded as the principal direction of cleavage. Twins occur according to OP, the individual crystals being grown together sometimes at the upper, sometimes at the lower end. From the results of corrosion-experiments, it appears that struvite is not hemihedral.

STRYCHNINE, $C^{21}H^{22}N^2O^2$. *Detection*.—For the detection of strychnine in chemico-legal investigations, J. St. Clair Gray (*Zeitschr. anal. Chem.* 1873, 125) triturates the suspected substances with water to a pulp, mixes this with excess of acetic acid, digests the mixture at 27° for about twenty-four hours; and then pours it into a dialyser. After forty-eight hours, the dialysate is evaporated down to a drachm and repeatedly shaken with chloroform. The aqueous solution is then made alkaline with ammonia, and again agitated with chloroform, and the residue left on evaporation may be examined for strychnine by the usual tests. According to J. B. Lyman (*ibid.* 126), potassium permanganate, silver oxide, and hydrated manganese dioxide produce with strychnine the same colour-reactions as chromates, and in many respects are even superior to the latter as tests for that alkaloid.

On the detection and separation of Strychnine in mixtures of Alkaloids, see **PLANT-BASES** (p. 1635).

Reaction of Strychnine with Nitric Acid.—When strychnine is added to nitric acid, and the liquid—on completion of the reaction, which is attended with copious evolution of nitrous fumes—is diluted with water, an amorphous body is thrown down, the solution of which in glacial acetic acid deposits, after dilution, a basic substance, perhaps consisting of nitrostrychnine. When strychnine is boiled for some time with strong nitric acid, and the solution is concentrated by evaporation, it deposits a crystalline acid having the composition $C^{16}H^{14}N^2O^{13}$, which melts with decomposition above 300° , and forms red amorphous salts (R. Schiff, *Gazz. chim. ital.* viii. 82).

Strychnine Tri-iodide, $C^{20}H^{22}N^2O^2.HI^3$, prepared by triturating 2 pts. strychnine with 1 pt. iodine, and crystallising the mixture from alcohol, forms violet needles resembling potassium permanganate, and is identical with that described by Tilden, and probably also with that obtained by Herapath (v. 441). It is unstable in solution, but in the solid state it may be heated without alteration to 135° . It dissolves with red colour in nitric and sulphuric acids, and when heated with alcoholic iodine-solution, appears to be converted into a higher iodine-compound (H. R. Bauer, *Arch. Pharm.* [3], v. 289).

Polyhydrosulphide, $C^{21}H^{22}N^2O^2.H^2S^3$. Hofmann, who obtained this compound by mixing a cold-saturated solution of strychnine in strong alcohol with an alcoholic solution of ammonium sulphide containing free sulphur, assigned to it the formula $C^{21}H^{22}N^2O^2.H^2S^3$ (vi. 1040). E. Schmidt (*Ber.* v. 1267) found that an alcoholic solution saturated with hydrogen sulphide deposited after some time orange-red needles, to which he assigned the formula $2C^{21}H^{22}N^2O^2.3H^2S^2$. Hofmann, however (*Ber.* x. 1087), finds that the compound prepared by Schmidt's method is identical in colour, composition, facility of decomposition, and chemical behaviour in general, with that obtained by his own. To determine which of the two formulæ above cited is the true representative of its composition, weighed quantities of the compound were treated with a solution of arsenic trioxide in hydrochloric acid, and the resulting precipitates were weighed and analysed; moreover, the polyhydrosulphide was decomposed with a solution of lead acetate in glacial acetic acid, and the resulting black precipitate was weighed. Numerous analyses showed that the arsenic precipitate has the composition As^2S^{13} , and is formed in quantity corresponding with the equation $3H^2S^2 + As^2O^3 = 3H^2O + As^2S^{13}$, and that the lead precipitate has the composition PbS^6 . Hence Hofmann now represents the polyhydrosulphide by the formula $(C^{21}H^{22}N^2O^2)^2.H^2S^6$, which agrees very closely with the results of the elementary analysis. The compound is probably however not a salt of the acid H^2S^6 , for although when decomposed by acids it yields a clear oil having a peculiar odour, and agreeing in its essential properties with hydrogen persulphide, it does not, on the other hand, yield by double decomposition any compounds that can be regarded as salts of the acid H^2S^6 . The polyhydrosulphide is most probably analogous in constitution to the periodides, and may perhaps be formulated as $2C^{21}H^{22}N^2O^2.H^2S^3.S^4$, in which case the oil separated from it by acids must be regarded as a solution of the additional sulphur in hydrogen disulphide. E. Schmidt, also (*Ber.* x. 1288), now admits the identity of Hofmann's polyhydrosulphide of strychnine, prepared by means of hydrogen sulphide, with his own compound obtained with ammonium sulphide, and attributes the inferior

stability of the latter to the circumstance that it separates in less compact crystals, which are, therefore more easily attacked by reagents. Compare BRUCINE HYDROSULPHIDES (p. 353).

Hydrates of Strychnine or Hydrostrychnines (Gal a. Etard, *Compt. rend.* lxxxvii. 362). Strychnine takes up 2 and 3 mols. H^2O , forming compounds which act as distinct bases, uniting with acids to form crystallisable salts. They are formed by heating finely pulverised strychnine with ten times its volume of cold-saturated solution of baryta for about forty hours at 135° – 140° in sealed tubes freed from air as completely as possible. The liquid freed from baryta by carbon dioxide, filtered in a stream of that gas, and distilled in a vacuum, finally deposits white crystals of dihydrostrychnine, $C^{21}H^{28}N^2O^4 = C^{21}H^{22}N^2O^2 \cdot 2H^2O$, which may be purified by recrystallisation from water. This compound forms microscopic prisms, dissolves easily in hydrochloric acid, forms a well-crystallised hydrochloride, and a sparingly soluble tartrate which also crystallises well. Trihydrostrychnine, $C^{21}H^{32}N^2O^5 = C^{21}H^{22}N^2O^2 \cdot 3H^2O$, contained in the mother-liquors of the preceding compound, forms yellowish prisms, and yields a well-crystallised tartrate.

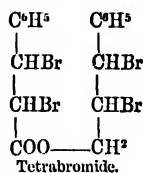
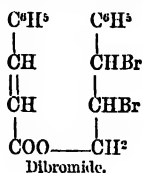
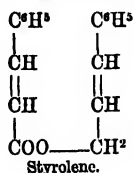
Both these bodies are moderately stable in the solid state, but extremely liable to alter in solution, especially the trihydro-compound, so that in their preparation, &c., it is necessary to protect them from the air as completely as possible. Both of them give a specular deposit with silver nitrate, and reduce the chlorides of gold and platinum, with violet coloration. They do not give the strychnine reaction with sulphuric acid and potassium chromate. They appear to possess the character of aldehydes, as is further shown by their behaviour with sodium bisulphite, and they are probably identical with Schützenberger's oxy- and dioxystrychnine respectively (iv. 320).

STRYCHNOS. The fat extracted by ether from the seeds of *Strychnos Nuxvomica* consists of the glycerides of oleic, palmitic, capric, caprylic, caproic, and butyric acids, and that of an acid containing 76.89 per cent. carbon, and having a melting point higher than that of stearic acid (F. Meyer, *Russ. Zeitschr. Pharm.* 1875, 417, 449).

STYCKERIN, $C^9H^{12}O^3 = C^6H^5 \cdot CHOH \cdot CHOH \cdot CH^2OH$. Syn. with PHENYL-GLYCEROL (p. 1562).

STYPNIC ACID, $C^6H(NO^2)^3(OH)^2$. Syn. with TRINITRORESORCINOL (p. 1750).

STYRACIN, STYRYL CINNAMATE, or CINNYL CINNAMATE, $C^{16}H^{16}O^2 = C^9H^{17}O^2 \cdot C^7H^9 = C^6H^5 \cdot CH=CH \cdot CO^2C^3H^9$. This compound is contained, together with styrolene, free cinnamic acid, and other bodies, in liquid storax, and may be separated therefrom by methods already described (i. 986). W. v. Miller (*N. Rep. Pharm.* xxiv. 1), after distilling off the styrolene with vapour of water, heats the resinous residue on the water-bath with one-tenth of its weight of crystallised sodium carbonate, till the mass no longer froths; decants the aqueous solution which contains the greater part of the free cinnamic acid in the storax; heats the residue with a solution of 1 pt. caustic soda in 40 pts. water to remove the rest of the cinnamic acid, and free the styracin from the greater part of the resin; treats the residue with cold alcohol, and crystallises the portion insoluble therein from hot alcohol. The crystals of styracin thus obtained are purified by pressure between filter-paper and further treatment with cold alcohol, which removes any portion of resin that may still adhere to them. The styracin thus obtained melts at 44° . It unites with bromine, yielding a dibromide and a tetrabromide, the latter in the form of a resin which has not been obtained pure. The constitution of styracin and its two bromine-compounds may be represented by the following formulæ:



The dibromide is converted by reduction into phenyl-propyl cinnamate [phenyl-acrylate], $C^6H^5 \cdot CH=CH \cdot COOC^3H^9(C^6H^5)$, and the tetrabromide into phenyl-propyl phenylpropionate, $C^6H^5 \cdot CH^2 \cdot CH^2 \cdot COOC^3H^9(C^6H^5)$. Styracin itself is but little inclined to take up hydrogen.

The action of bromine on phenyl-propyl cinnamate in ethereal solution gives rise

to phenyldibromopropyl cinnamate, $C^6H^7.COOCC^6H^4Br^2(C^6H^5)$, and other products still richer in bromine. By the prolonged action of bromine-vapour, phenylpropyl cinnamate is converted into styracin tetrabromide (W. v. Miller, *Liebig's Annalen*, clxxxviii. 184).

STYROCAMPHENE. See STORAX (p. 1827).

STYROLENE, C^8H^8 . Syn. with CINNAMENE (p. 497). It is formed, together with benzene, naphthalene, phenanthrene, and anthracene, by passing a mixture of ethylene and diphenyl vapour through a porcelain tube heated to bright redness (Barbier, *Compt. rend.* lxxix. 660). On its occurrence in Storax, see p. 1827.

A compound of styrolene with acid sodium sulphite, $C^8H^8.NaHSO^3$, is formed by heating 1 mol. styrolene (from cinnamic acid) for several hours with a solution of 1 mol. of the acid sulphite (concentration 2 : 5), best at about 120° . It crystallises from water in nacreous laminae, melts at 306° , dissolves easily in water and in hot alcohol, and is soluble also in ether. Styrolene obtained from liquid storax, or by distillation of metastyrolene, appears to react with sodium bisulphite somewhat differently from that which is prepared from cinnamic acid, yielding, when heated with the bisulphite solution at 110° , small quantities of crystals different in appearance from those above described; moreover, the most favourable temperature for the formation of the crystals in the preparation from styrolene obtained from liquid storax or from metastyrolene is about 155° (W. v. Miller, *N. Rep. Pharm.* xxiv. 31).

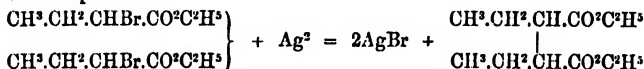
STYROLENE ALCOHOL, $C^8H^{10}O^2 = C^6H^5.CHOH.CH^2OH$. Syn. with PHENYLGLYCOL (p. 1563).

SUBERIC ACIDS, $C^8H^{14}O^4$. Ordinary suberic acid (m. p. 140°), originally obtained by oxidising cork with nitric acid, is also produced by the action of fuming nitric acid at temperatures not exceeding 110° , on paraffin (p. 1489).

The two following acids, isomeric with it, have been obtained synthetically :

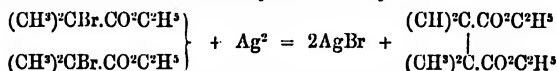
(1). Diethyl-succinic acid, $\begin{array}{c} CH^3.CH^2.CH.CO^2H \\ | \\ CH^3.CH^2.CH.CO^2H \end{array}$. The ethylic ether of this acid

is obtained by heating ethyl α -bromobutyrate or α -iodobutyrate at 120° – 130° in a sealed tube with finely divided silver and methyl iodide, which latter assists the reaction, but takes no direct part in it :



It boils, after rectification, at 233° – 235° (C. Hall, *Ber.* vi. 28).

(2). Tetramethyl-succinic acid, $\begin{array}{c} (CH^3)^2C.CO^2H \\ | \\ (CH^3)^2C.CO^2H \end{array}$. The ethylic ether of this acid is produced in like manner from ethyl bromisobutyrate :



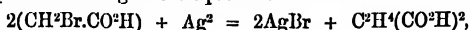
By subjecting the product to repeated fractional distillation, the ethylic tetramethylsuccinate is obtained as a liquid boiling at 230° – 231° (uncorr.), and having a sp. gr. of 1.012 at 0° , 1.0015 at 13.5° . The suberic acid obtained from it forms, after three crystallisations from hot water, small, hard, frequently spherical groups of crystals, apparently consisting of quadratic tablets with pyramidal summits. It melts at 95° , and resolidifies at a somewhat lower temperature. It is not volatile at ordinary temperatures, very slightly at 100° , but sublimes at higher temperatures in broad feathery laminae. It is extremely soluble in alcohol, ether, and hot water, less soluble in cold water, 100 pts. water at 11° dissolving 2.2 pts. of it. The ammonium, potassium, and sodium salts are also very soluble; the barium, calcium, and lead salts are white bulky precipitates; the copper salt is a bluish-green precipitate; the silver salt a white precipitate which quickly turns brown on exposure to light, and dissolves in 2,500 pts. water at 10° (Hell a. Wittekind, *Ber.* vii. 319).

SUCCINIC ACID, $C^4H^4O^4 = \begin{array}{c} CH^2.COOH \\ | \\ CH^2.COOH \end{array}$. This acid has been found in the

juice of unripe grapes gathered in June (Brunner a. Brandenburg, *Ber.* ix. 982); also among the products of the schizomycetic fermentation of mannitol (p. 777), and in urine after asparagus has been eaten (Hilger, *Liebig's Annalen*, clxxi. 208).

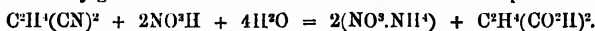
Succinic acid is formed : α . By the oxidising action of dilute nitric acid on normal

butyric acid, and, together with acetic acid, by the action of the same acid on normal caproic acid; but in both cases, unless special precautions are taken, the action goes further, and the succinic acid is oxidised to carbonic acid and water (Erlenmeyer, Sigel & Belli, *Ber.* vii. 696). β . By heating ethyl chlorocarbonate, bromacetic acid, and finely divided silver in molecular proportions at 130° in a sealed tube. The reaction takes place according to the equation:



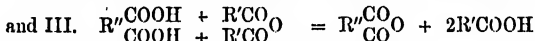
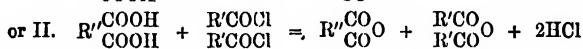
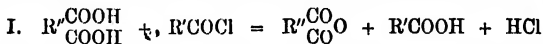
the chlorocarbonic ether taking no direct part in it, but being resolved into CO^2 and $\text{C}^2\text{H}^4\text{Cl}$. A fetid brominated liquid is formed as a secondary product (A. Stelzner, *Ber.* vi. 184).

The preparation of succinic acid from ethylene cyanide by decomposition with alcoholic potash (Simpson's method, v. 454) takes a long time when large quantities of material are operated on; and, according to Jungfleisch (*Bull. Soc. Chim.* [2], xix. 197), the conversion of the ethylene cyanide into succinic acid may be much more quickly effected by gradual addition of nitric acid diluted with an equal bulk of water:



The use of nitric acid has the further advantage of decomposing colouring matters which would otherwise contaminate the product.

Reactions. 1. Succinic acid, like other diatomic bibasic acids, is converted by the action of acetyl chloride, benzoyl chloride, succinyl chloride, and acetic anhydride into the corresponding anhydride, the reactions being represented by the following general equations:



In this manner succinic acid and isodibromosuccinic acid are easily converted into anhydrides by acetyl chloride at ordinary temperatures; isosuccinic acid, $\text{CH}^3.\text{CH}(\text{CO}^2\text{H})^2$, and ordinary dibromosuccinic acid, are not attacked; succinyl chloride and succinic acid yield succinic anhydride; and *acetic anhydride*, heated for several hours in sealed tubes (mostly at 125° – 150°) with succinic and isodibromosuccinic acid, converts them into their anhydrides. Ordinary dibromosuccinic acid, heated with acetyl chloride, yields acetyl bromide, acetic acid, and monobromomaleic anhydride (Anschütz, *Ber.* x. 325, 1881).

On the reaction of Succinic acid with *Paraphenylenediamine*, see PHENYLENE-DIAMINES (p. 1560); with *Phthalic Anhydride* (p. 1615).

SUGARS. *Distribution in Plants.*—V. Jodin (*Ann. Chim. Phys.* [5], 491), from a comparison of the known facts relating to the distribution of sugars in the vegetable kingdom, has arrived at the following conclusions:

1. A great number, if not all, the plants belonging to the higher classes contain, distributed through their organisms, sugar consisting of a mixture of saccharose and inverted sugar.

2. In the same plant the average amount of sugar in the leaves is very small, but it attains its maximum in the flowers, fruits, stems, and roots, which possess the chlorophyllic function in a slight degree only.

3. The smallness of the quantity of sugar in the leaves cannot be regarded as evidence against the direct production of sugar by these organs.

4. The constant presence of a certain quantity of sugar in fungi appears to prove that the glycogenic and chlorophyllic functions are independent of each other. In the green leaf these two functions exist together, but are not mutually dependent.

The quantity of sugar contained in the 'nectar' of various flowers (the sweet-tasting liquid secreted within the cups of flowers which are fertilised by insects) has been determined by A. S. Wilson, with the following results:

	Total mgm.	Fruit- sugar	Cane-sugar (as fruit-)
1. Fuchsia, per flower	7.59	1.69	5.9
2. <i>Claytonia Alsinoïdes</i> , ditto	0.413	0.175	0.238
3. Everlasting pea, ditto	9.93	8.83	1.60
4. Vetch (<i>Vicia Cracca</i>) per raceme	3.16	3.16	0.01
5. Ditto, per single flower	0.158	0.158	—
6. Red clover, per head	7.93	5.95	1.98
7. Ditto, per floret	0.132	0.099	0.033
8. Monkshood, per flower	6.41	4.63	1.78

Saccharose, Cane-sugar, Beet-sugar. This kind of sugar exists, together with dextrose, in vine-leaves. In one experiment a kilo. of the leaves yielded 9.2 g. saccharose and 26.5 g. dextrose; in another, more quickly carried out, 15.80 saccharose and 17.49 glucose. Cherry and plum leaves were also found to contain both kinds of sugar; 1 kilo. of plum-leaves gave 33 g. saccharose and 12 g. dextrose (Petit, *Compt. rend.* lxxvii. 944). Researches on the distribution of saccharose in the sugar-beet have been published by C. Violette (*Compt. rend.* lxxix. 899; *Ann. Chim. Phys.* [5], iii. 546; *Chem. Soc. J.* 1875, 376).

Specific Gravity.—According to Maumené (*Bull. Soc. Chim.* [2], xxii. 23), the specific gravity of cane-sugar is 1.5951 at 15°, whereas former determinations gave 1.606 (v. 470). The dissolution of sugar in water is attended with diminution of volume, unless the sugar and water are brought together in equal proportions by weight. With excess of water, contraction takes place; with excess of sugar, expansion; both however in small proportion only.

Solubility in Water.—According to Courtonne (*Compt. rend.* lxxxv. 959), 100 g. water at 12.5° dissolve 198.547 g. cane-sugar, a result agreeing very nearly with the proportion 1 : 2 found by Berthelot and by Scheibler, not with Maumené's result (1 : 3). At 45°, 100 g. water dissolve 245 g. sugar.

On the Crystallisation of Cane-sugar on the large scale (preparation of sugar-candy), see Weitz (*Dingl. ccxxxi.* 452; *Chem. Soc. J.* xxxvi. 844).

Reactions.—1. When well-dried ammonia-gas is passed over perfectly dry saccharose, the sugar becomes opalescent at first, and viscid after about twelve hours. The maximum amount of ammonia taken up is 7.83 per cent. by weight of the sugar, but part of this is given off when the strength of the current of gas is diminished, and when the sugar is exposed to the air, the increase of weight sinks to 1.2 per cent. After three months the sugar was found to retain 0.37 per cent. ammonia, and to have a strong bitter taste (E. Laborde, *Compt. rend.* lxxviii. 82).

2. **Conversion into Glucose.**—Experiments by H. Pellet (*Ann. Chim. Phys.* [5], xiii. 394) on the action of various substances on cane-sugar as influenced by temperature and the duration of the action, have led to the following conclusions:

(1). Under the influence of heat, weak solutions of saccharose alter more rapidly than concentrated solutions.

(2). Glucose assists in the transformation of saccharose into glucose, in proportion to its pre-existing quantity, but its action becomes *nil* when the sugar-solution is saturated (Gunning).

(3). Mineral salts act strongly on saccharose at a certain temperature. Chloride of potassium appears to be more energetic in its action than the nitrate. Ammonium nitrate has a very energetic action. By boiling for thirty minutes a mixture of 100 c.c. of water, 10 grams of sugar, and 5 grams of ammonium nitrate, all the sugar is transformed into glucose.

(4). Organic salts have a very weak action.

(5). The quantity of glucose found in the molasses from the refinery is determined by the total influence of time, heat, and mineral salts, in addition to the quantity of glucose pre-existing in the unrefined sugar.

3. **Inversion and Fermentation.**—Cane-sugar is readily inverted by certain ferments, such as *Penicillium glaucum* and *Aspergillus niger*; several species of *Mucor*, however (*M. mucedo*, *M. circinelloides*, &c.), have no action upon it. Two species, *M. spinosus* and *M. circinelloides*, resemble one another in their action on beer-wort, but the second is much the more active. When these bodies are placed in liquids destitute of free oxygen, their mycelium takes the form of cells which multiply with great rapidity; the mycelium, however, reverts to the ordinary form directly the liquid is aerated. In solutions of dextrose and levulose, alcoholic fermentation is set up, as in beer-wort, but in a solution of cane-sugar there is no fermentation; if, however, spores of *Torulas*, or of any other ferment capable of inverting cane-sugar, be added, the ordinary alcoholic fermentation commences. Hence it appears that cane-sugar is not directly fermentable (U. Gayon, *Compt. rend.* lxxxvi. 52).

Detection.—To detect sugar in glycerin, R. Böttger (*Zeitschr. anal. Chem.* x. 508) mixes 5 drops of the glycerin with 100 drops of distilled water, 1 drop of nitric acid of sp. gr. 1.3, and 30 to 40 mg. ammonium molybdate, and boils the mixture. If sugar is present, the liquid assumes a deep blue colour.

Estimation.—1. By **Ferric Chloride.** The property of sugar to prevent the precipitation of ferric chloride by ammonia may be made available for the estimation of sugar. 100 milligrams of iron in the state of ferric chloride require 2.587 g. sugar to keep the liquid clear on addition of ammonia. Accordingly, to this quantity of the sugar to be examined—after addition of ammonium oxalate to separate any lime

that may be present—ammonia is added in excess, and then solution of crystallised ferric chloride as long as the liquid remains clear. The number of mgm. of iron added without the formation of a precipitate will then give the percentage of real sugar in the sample: the solution must not be heated. If the ferric chloride has been decomposed by prolonged heating at 100°, 2·710 g. sugar will be required to keep 100 mgm. iron in solution. As invert-sugar acts much more strongly in this way than crystallisable sugar (0·387 g. saccharose after inversion acting as strongly as 2·587 g. before inversion), the saccharose must, previous to titration, be freed from invert-sugar by treatment with cold alcohol (E. Riffard, *Compt. rend.* lxxvii. 1103).

2. C. Nicol (*Zeitschr. anal. Chem.* 1875, 179) finds by comparative experiments that the inversion of sugar, with a view to its determination by Fehling's solution, is best effected by heating it in sealed tubes at 130°, the inversion being then complete either with or without the addition of an acid, whereas if the sugar is heated in an open vessel, the addition of an acid is necessary. No difference was observed between the action of sulphuric and that of hydrochloric acid.

On the comparative merits of various methods of estimating cane-sugar, see G. C. Stewart (*Chem. News*, xxxi. 212, 223), H. C. Humphrey (*Amer. Chemist*, vi. 203; *Chem. News*, xxxiii. 205). A table of the properties of different varieties of cane-sugar, founded on an investigation by Lotmann, is given by R. F. Smith (*Chem. News*, xxxiii. 225). On the estimation of sugar in coloured liquids containing glucose, see Pellet a. Parquier (*Monit. scient.* [3], vii. 1074; *Jahresb. f. Chem.* 1877, 1193).

Estimation of the yield of Pure Crystallisable Sugar from various raw Beet-sugars. C. Scheibler (*Zeitschr. des Vereins für die Rübenzucker-industrie*, 1872, 297; *Dingl. pol. J.* cxi. 48) describes an improved method of carrying out the process devised by Payen in 1846, by which the syrup adhering to the already crystallised sugar is removed by washing with an acid saturated solution of sugar in alcohol of about 85 per cent. For Payen's single washing fluid and tared filter, Scheibler substitutes the following fluids and apparatus:—(1). Alcohol of 99–100 per cent.; (2). Alcohol of 96 per cent. saturated with sugar; (3). Alcohol of 92 per cent. also saturated; and (4). Alcohol of 85 per cent. mixed with 5 vols. per cent. of ordinary acetic acid and saturated with sugar. About 20 grams of the sugar to be tested is weighed into tared tubes about 2 centimeters wide and 15 centimeters long, having a narrow tube fused on to them at one end, and containing a plug of felt or cotton-wool just above the junction of the wide and narrow portions. These tubes are connected by their narrow ends with bottles, in which a partial vacuum can be created by some convenient means, such as a Bunsen water-pump, while their wide upper extremities are closed by corks carrying two tubes, one of which serves for the admission of dry air, and the other (carrying a stopcock) for the introduction of the washing fluids by means of a pipette. The sugar is first covered with absolute alcohol and left to stand for fifteen minutes; this liquid is drawn off and replaced by No. 2, which is followed by No. 3, and then by No. 4. This last, which is the effective solvent of the syrup, is left on the sugar for fifteen or twenty minutes, and is then allowed to run off slowly; more is added and run off, and so on, till the sugar imparts no more colour to the liquid. The remaining portions of (4) are then displaced by the other liquids, used in reverse order, and the nearly pure sugar left is dried by passing air through it while the tube is surrounded by a metallic casing filled with steam. The weight of the residue so obtained is obviously that of the sugar which existed ready crystallised in the original specimen plus sand and other impurities insoluble in spirit. It is now only necessary to 'polarise' this residue to determine the quantity of sugar which it contains, and so obtain all the data required to ascertain how much crystallised sugar was contained in the original.

Estimation of Saccharose in Coloured Liquids containing Glucose.—The following method is recommended by Pellet a. Parquier (*Monit. scient.* [3], vii. 1074). (1). 100 grams of the liquid under examination (molasses) are diluted with water to a total volume of 500 c.c. (2). 100 c.c. of this liquid are mixed with 40 c.c. of a solution of lead acetate (sp. gr. 1·150–1·200) diluted with water to 200 c.c. and filtered. (3). Of this filtrate, 100 c.c. are mixed with 10 c.c. acetic acid, and examined in the saccharimeter, the observed rotation being reduced to 100 c.c. of the normal liquid, and the sugar calculated for 100 g. of normal molasses. (4). 50 c.c. of the liquid obtained as in (2) are mixed with 10 c.c. hydrochloric acid, inverted at 70°; slightly supersaturated with soda when cold; acidulated with acetic acid; diluted to 100 c.c.; mixed (if too strongly coloured) with 1 g. animal charcoal; filtered; introduced into the saccharimeter; the temperature determined; and the quantity of crystallisable sugar calculated according to the following formulæ (the first applying to Soleil's, and the second to Laurent's saccharimeter), in which S denotes the sum of the saccharimetric readings

before and after inversion—i.e. the entire diminution of rotation—and T the temperature of the inverted solution at the time of observation:

Formula for Soleil:

$$P = \frac{200 S}{288 - T} \text{ and } \frac{P \cdot 16 \cdot 35}{100} \text{ or } P \cdot 0 \cdot 1635 = \text{Sugar for 100 c.c.}$$

Formula for Laurent:

$$P = \frac{200 S}{288 - T} \text{ and } \frac{P \cdot 16 \cdot 20}{100} \text{ or } P \cdot 0 \cdot 1620 = \text{Sugar for 100 c.c.}$$

(5). To determine the normal glucose, 10 c.c. of No. 2 are mixed with sodium carbonate and diluted to 100 c.c., of which 30 c.c. are to be mixed with 30 c.c. copper solution, warmed in the water-bath, and the copper precipitate weighed. (6). To estimate the total sugar, 10 c.c. of liquid No. 2 are mixed in a flask of 250 c.c. capacity with 10 c.c. sulphuric acid (100 g. H^2SO^4 in the litre) and 50 c.c. water; the mixture is heated in the water-bath for half to three-quarters of an hour, then diluted to 250 c.c.; the total glucose estimated as above in 30 c.c. of the liquid, after cooling, and calculated to 100 g. of the molasses; the original amount of glucose deducted; and the difference calculated to crystallisable sugar. The ratio of the normal glucose to the difference between the crystallisable sugar determined by the saccharimeter and that determined by the copper solution, affords the means of estimating the rotatory power belonging to the reducing sugar.

On the Estimation of Saccharose and Glucose by the Optical Saccharimeter, see Landolt ('Das optische Drehungsvermögen Organischer Substanzen,' Braunschweig, 1879, 148–188).

Sugar manufacture.—On the Refining of Sugar, see Wichelhaus (*Neue Zeitschrift für die Rübenzucker Industrie*, 1878, 177–318; *Jahresb. f. Chem.* 1879, 1149; *Chem. Soc. J.* xxxiv. 690); by the use of Alumina: Kohlrausch (*Chem. Centr.* 1878, 185).

Purification of Syrups by boiling with dilute Sulphuric and Hydrochloric acid; Margueritte (*Dingl. pol. J.* cex. 327; *Jahresb. f. Chem.* 1874, 1167); by Ammonium Phosphate and Baryta: P. Lagrange (*Compt. rend.* lxxvii. 1245; *Chem. Soc. J.* xxvii. 209; *Jahresb.* 1873, 1072; 1874, 1169); by Phosphoric acid: Vibrans (*Dingl. pol. J.* ccxxi. 387, 579; *Jahresb.* 1876, 1138); by Calcium Borate: Lecale a. Gaudry (*Dingl. ccxx. 154; Jahresb.* 1876, 1139).

Decalcification of Syrups by Phosphoric acid: Scheibler (*Dingl. pol. J.* ccxxi. 257; *Chem. Soc. J.* xxvii. 1189; *Jahresb.* 1874, 1167).

Purification of Beet-juice with Barium Carbonate and Hydrate: Lagrange (*Compt. rend.* lxxx. 397; *Jahresb.* 1875, 833).

Recovery of Crystallisable Sugar from Molasses: H. Schwarz (*Dingl.* ccxxvi. 182; *Jahresb.* 1877, 1189; *Chem. Soc. J.* xxxiv. 179); Drevermann (*Chemische Industriezeitung*, 1878, 214; *Jahresb.* 1878, 1151); Zenisek (*Jahresb.* 1878, 1152). Recovery from Calcium Sucrates: Drevermann (*Chem. Centr.* 1879, 46); Stiffens, Manoury, Mateyczek a. Drevermann (*Chem. Centr.* 1879, 269; *Jahresb.* 1878, 844).

Effect of Salts on the Crystallisation of Sugar: Durin (*Compt. rend.* lxxxi. 621; *Jahresb.* 1875, 1126); Lagrange (*Dingl.* ccxix. 363; *Jahresb.* 1876, 1138).

2. **Lactose**, or **Milk-sugar**, $C^{12}H^{22}O^{11}$. This sugar, when boiled with dilute sulphuric acid ($\frac{1}{2}$ acid diluted with 2 vols. water), the water being continually renewed as it evaporates, till a light brownish coloration is produced, splits up into two sugars or glucoses, $C^6H^{12}O^6$, viz. Dextrose and Galactose. To separate these, the solution is neutralised with calcium carbonate, mixed with baryta water, then treated with carbon dioxide, concentrated, left to crystallise slowly, and finally mixed with alcohol, whereupon the galactose separates in the form of a crystalline mass; and the mother-liquor, especially on addition of absolute alcohol, yields a second crystallisation, consisting of dextrose. The separation of these glucoses may also be effected by means of alcohol of 95–98 per cent., in which the latter is the more soluble of the two.

Galactose crystallises in prisms, melts at 118° – 120° in the air-dried state, at 142° – 144° after drying at 100° . It reduces only 4 mols. cupric sulphate, whereas dextrose reduces 5 mols. By oxidation with nitric acid it is converted into mucic acid. Heated at 160° for twenty-four hours with acetic anhydride, it is converted into pentacetyl-galactose, $C^6H^7(C^2H^3O)^5O^6$, a pale gum-like substance, which softens at 62° , and melts at 66° – 67° . The dextrose from milk-sugar was at first regarded as a distinct modification, and called *Lactoglucose*; but subsequent experiments have shown that it is identical with grape-sugar. It melts in the air-dried state at 70° – 71° , and at 132° – 136° after drying at 100° (Fadarkowski, *Ber.* ix. 42, 278; xi. 1069).

Synthesis of Lactose.—When the mixture of galactose and dextrose obtained

as above is heated to boiling with 3 pts. of acetic anhydride (b. p. 146° – 150°) in a reflux apparatus till the mass is completely dissolved, and the product is then treated with water, a viscid ether is formed having the composition $C^{12}H^{22}O^{11} = C^{12}H^{14}(C^2H^3O)^6O^{11}$, and identical with that which Schützenberger obtained by heating milk-sugar with excess of acetic anhydride (vi. 1045). The two products agree in melting point (52°), and in specific rotatory power, the other prepared as above giving $[\alpha]_D = +30.2^{\circ}$, Schützenberger's ether $+31^{\circ}$; both readily give off acetic acid when exposed to the air, and when saponified with alkalis yield one and the same product, viz. milk-sugar. The specific rotatory power of the lactose thus obtained from the other prepared as above described was found to be $[\alpha]_D = +56.7^{\circ}$, that of natural milk-sugar being $+56.4^{\circ}$. The synthetically prepared lactose, heated for two hours at 140 – 145° , yielded an anhydride, $C^{12}H^{22}O^{11}$, having a specific rotatory power $[\alpha]_D = 60.05^{\circ}$; that of dehydrated milk-sugar is, according to Biot, $[\alpha]_D = +60.28^{\circ}$; according to Berthelot, $+59.3^{\circ}$ (Demole, *Ber.* xii. 1936).

On the Alcoholic Fermentation of Milk-sugar, see MILK (p. 1325).

3. **Maltose**, $C^{12}H^{22}O^{11} + H^2O$. This isomeride of saccharose and lactose is the final product of the action of malt-extract on starch. It is less soluble in alcohol than dextrose, has a specific rotatory power of $+154$ to $+155^{\circ}$ for the transition-tint, and its empyric oxide reducing power is to that of dextrose in the ratio of 62 or 63 to 100. By the prolonged action of acids it is converted into dextrose (O'Sullivan, *Chem. Soc. J.* xxv. 579; xxxv. 771). See also STAUCH (pp. 1821–1823).

4. **Melezitose**, $C^{12}H^{22}O^{11}$. This kind of sugar, first obtained from the manna of various species of *Eucalyptus* growing in Tasmania (vii. 869), has also been obtained from a *Persina manna*, originating from a leguminous plant called *Palhagi Maurorum*. The aqueous extract of the manna evaporated to a syrup and treated with animal charcoal, yields, after several months, a crop of monoclinic crystals which, after recrystallisation from alcohol of 60 per cent., are quite pure, and have the composition $C^{12}H^{22}O^{11} + H^2O$. The water of crystallisation escapes readily at 100° , or in a vacuum over sulphuric acid, slowly at ordinary temperatures.

Melezitose melts at a temperature a little above 140° , and has a dextrorotatory power of $94^{\circ} 48'$ for the transition-tint, $88^{\circ} 5'$ for the line D. When boiled with dilute acids, it yields nothing but dextrose; with nitric acid it gives oxalic but no mucic acid.

The manna above mentioned was found to contain also saccharose and a syrupy sugar which reduced Fehling's solution, but was not fermentable. The saccharose was extracted by dissolving the mother-liquor of the melezitose in alcohol, and adding ether till the solution became turbid, the saccharose then crystallising out after a few days (A. Villiers, *Cempt. rend.* lxxxiv. 35; *Ann. Chim. Phys.* [5], xii. 43).

5. Another sugar isomeric with saccharose is formed when a solution of perfectly pure glucose in absolute alcohol, well cooled with ice, is saturated in the dark with dry hydrogen chloride. The saturated solution is heated; the acid evaporated in a vacuum over sulphuric acid; the coloured syrup is saturated with caustic baryta, and repeatedly dissolved in alcohol of 94 per cent.; and the solution, after being left to evaporate without heating, is treated with ether to remove a substance having a strong bitter taste. The sugar thus obtained is colourless, has the aspect and taste of gum, is very hygroscopic, and dissolves very readily in water. At 100° it gives off $\frac{1}{20}$ of its weight of water, and becomes hard and transparent; but to obtain it perfectly anhydrous, it must be dried for several days at 130° in a stream of carbon dioxide. It is not fermentable. Its aqueous solution does not reduce Fehling's liquid. When heated at 160° , it decomposes according to the equation $C^{12}H^{22}O^{11} + H^2O = 2C^6H^{12}O^6$, yielding a sugar having the composition of glucose, but not identical therewith, inasmuch as, though it reduces a solution of copper, it has a very sweet taste and is very difficult to ferment. The compound $C^{12}H^{14}(C^2H^3O)^6O^{11}$ which Schützenberger obtained by heating cane-sugar with a large excess of acetic anhydride (vii. 1195), is perhaps the octaacetyl-derivative of this sugar, its formation being analogous to that of the aldanes (vii. 32) from the aldehydes of the fatty series (Gautier, *Bull. Soc. Chim.* [2], xxxii. 33).

Glucoses, $C^6H^{12}O^6$. **Dextroglucose or Dextrose.** *Occurrence.*—According to E. Mach (*Dingl. pol. J.* cccxxv. 470), the sugar of the grape in the unripe state is chiefly dextrose; at the time of the general gathering it is almost wholly invert-sugar, while during the time of over-ripening the levulose becomes predominant. During fermentation the levulose is first attacked, afterwards the dextrose; cane-sugar added to the mixture remains unaltered till the middle of the fermentation, and then disappears. Must of wine mixed with cane-sugar yields a levorotatory wine; must mixed with grape-sugar, a dextrorotatory wine.

Dextrose occurs in *cinchona barks*, probably as a decomposition-product of quino-tannic acid (Carles, *Pharm. J. Trans.* [3], iii. 643).

Formation and preparation from Saccharose.—Durin (*Compt. rend.* lxxxvii. 754) finds by direct experiment that the conversion of the saccharose of sugar-juices into glucose is due, not to fermentation, but to purely chemical action, and that it is accelerated by heat. The presence of previously formed glucose has no influence on the result, but the reaction of the solution is of importance, the conversion being much quicker in acid or neutral than in alkaline solutions.

Neubauer (*Zeitschr. anal. Chem.* 1876, 188) prepares pure dextrose by adding white cane-sugar in fine powder by successive portions to a mixture of 500–600 c.c. alcohol of 80 per cent. and 30–40 c.c. fuming hydrochloric acid. The liquid when saturated is poured off, and left to crystallise in a covered vessel; and the crystals of dextrose thus obtained are washed with alcohol till the liquid runs off neutral, then dried, and recrystallised from boiling alcohol.

According to O. Hesse (*Lieb. Ann.* xcii. 169), the melting points of glucoses of various origin are not identical, but are always comprised between the limits 80° and 84°. *Honey-sugar* melts at 83°. *Starch-sugar*, after purification with alcohol and water, agrees with honey-sugar in every respect. On the rotatory power of these sugars, see p. 1221.

Sodium-glucose, $C^6H^{11}NaO^6$, is obtained on adding sodium ethylate to a solution of dextrose in absolute alcohol, as a white bulky precipitate, which, when quickly filtered, washed with absolute alcohol, and dried over sulphuric acid, forms a white or yellowish-white powder, extremely hygroscopic, soon becoming glutinous when exposed to the air, and apparently decomposing into sodium hydroxide and glucose. When heated in a stream of hydrogen at the temperature of the water-bath, it gives off 2 mols. water, and yields a brown amorphous mass, the formation of which begins at a temperature a little above 70°. Sodium glucosate dissolves in an alcoholic solution of bromine, yielding bromoform, and the compound $C^{12}H^{22}O^{12}NaBr$, which separates after a while in white laminar crystals (Hönig u. Rosenfeld, *Ber.* x. 871).

Acetonitrose, $C^6H^7(C^2H^3O)^4O^5NO^3$, is formed by the action of fuming nitric acid on acetochlorhydrose, $C^6H^7(C^2H^3O)^4O^3Cl$, the product of the action of acetyl chloride on glucose (vii. 12). The acetochlorhydrose required for the purpose need not be quite pure, but merely freed from acetic acid by heating it to 120°, and passing a stream of air through it. It is then to be mixed in a vessel cooled by ice, with 15 to 20 times its volume of fuming nitric acid, and the mixture, after standing for several hours, poured into ice-cold water. White flocks are then deposited, quickly changing to a heavy powder, which may easily be freed from a small quantity of unaltered acetochlorhydrose by crystallisation from ether and alcohol. Acetonitrose crystallises in white oblique prisms, or large rhombic plates. It is tasteless, insoluble in water, sparingly soluble in alcohol and ether, not explosive by heat or by percussion. It melts at 145°, has a density of 1.3487 at 18°, and is dextrogyrate, $[\alpha]_D = +159$. Heated to 100° in aqueous or alcoholic solution, it is converted into a body which reduces copper-solution, and is blackened by alkalis. Nascent hydrogen decomposes it with evolution of ammonia (A. Colley, *Compt. rend.* lxxvi. 437).

Detection.—For the detection of dextrose in presence of dextrin and allied bodies, C. Barfoed (*Zeitschr. anal. Chem.* 1873, 27) uses a solution of cupric acetate, which, when mixed with a solution of dextrose, gives, after a short time, a precipitate of cuprous oxide, whereas a solution of dextrin similarly treated remains unaltered for several days. Moreover, a solution of cupric acetate, very slightly acidulated with acetic acid, gives when boiled with dextrose and left to stand for a short time, a precipitate of cuprous oxide, whereas pure dextrin gives no reduction. Gum, cane-sugar, and milk-sugar behave in the same manner as dextrin. Barfoed points out that the ordinary methods of testing dextrin for dextrose are untrustworthy, inasmuch as Fehling's solution is reduced at ordinary temperatures even by very weak solutions of dextrin.

To detect glucose in presence of saccharose, R. Böttger (*J. pr. Chem.* lxx. 432) mixes the liquid with an equal volume of sodium carbonate solution (1 pt. of the crystallised salt to 3 of water), adds a pinch of *basic bismuth nitrate*, and heats the liquid to the boiling point. Under these circumstances, the slightest blackening or grey coloration of the bismuth-salt may be regarded as a sure indication of the presence of glucose. In the application of this test to the detection of glucose in urine and other animal fluids, or in vegetable juices, the blackening of the bismuth may arise from the action of sulphur resulting from the decomposition of albuminoids. To eliminate this source of error, E. Brücke (*Wien. Akad. Ber.* 1876, 52) makes use of a solution of *potassium-bismuth nitrate*, which precipitates albumin and its derivatives. This reagent is prepared by dissolving *basic bismuth nitrate* in a hot solution of potassium iodide, with addition of hydrochloric acid. The liquid under examination is acidulated with the same acid, then treated with the reagent, and filtered. The

filtrate should not be clouded either by a drop of dilute hydrochloric acid or by a drop of the test-liquid. This condition being fulfilled, the liquid is to be supersaturated with a concentrated alkali-solution, whereby a white flocculent precipitate is produced, and boiled. The presence of glucose will then be indicated by a blackening of the liquid from reduced bismuth.

Estimation.—(a). By *Fehling's Solution*.—C. Kraus (*Zeitschr. anal. Chem.* 1878, 323) mixes a measured volume of the sugar-solution with excess of Fehling's solution, and collects the separated cuprous oxide on a filter, dissolves it, after washing, in nitric acid, supersaturates with ammonia, and titrates with potassium cyanide. F. Mohr (*ibid.* 296) proceeds in the same manner, excepting that he oxidises the cuprous oxide with ferric sulphate or solution of iron-alum, and determines the resulting ferrous sulphate by titration with a normal solution of potassium permanganate.

Loiseau points out (*Compt. rend.* lxxvi. 1602) that the estimation of small quantities of dextrose by Fehling's solution may become inexact if the liquid contains a considerable quantity of caustic soda. If the sugar-solution be added by drops to the strongly alkaline copper-solution, a larger quantity of it will be required to destroy the blue colour than when the titration is quickly performed. If the separated cuprous oxide be boiled with strong soda-ley, and the liquid then left at rest for some time in contact with the air, it will recover its blue colour. Water alone, and a solution of normal sodium tartrate, do not exhibit this reaction. These sources of error may be avoided by reducing the alkalinity of the solution to such a point that 1 litre of the copper-solution shall be neutralised by 240 c.c. of decinormal sulphuric acid.

Boivin a. Loiseau (*Compt. rend.* lxxix. 1263) observe that Fehling's solution, when diluted with distilled water and boiled, deposits cupric oxide, and becomes more or less decolorised, but that this decoloration does not take place when river-water (Seine-water) is used instead of distilled water. They attribute the decoloration to a dissociation of the alkaline copper-solution by the pure water, which is prevented by the presence of a small quantity of soluble salts. G. Missaghi (*Gazz. chim. ital.* 1875, 414) suggests, as a more rational mode of preventing the decomposition in question, the addition of a few drops of a solution of tartaric acid or Rochelle salt to the reagent.

Champion a. Pellet (*Compt. rend.* lxxx. 181) attribute the non-decoloration of the solution in presence of certain salts, especially calcium salts, to the formation of a blue precipitate, which indeed is easily proved by adding a sufficient quantity of the salt and filtering, the liquid then running through colourless. Salts which, like the chlorides of potassium and sodium, give rise to the formation of cupric chloride, produce on boiling a greenish tinge in the liquid.

Possoz (*Compt. rend.* lxxv. 1836) observed that Fehling's solution, when it contains excess of alkali, precipitates cane-sugar as well as glucose. To prevent this, he mixes the solution with an alkaline bicarbonate, or passes carbon dioxide into it. The resulting solution of potassio-cupric tartrate + alkali-carbonate has no action on cane-sugar at 60°–90°, and may therefore be used for the estimation of glucose in presence of cane-sugar. The liquid to be tested is mixed with this solution, and kept for about three-quarters of an hour at 75°; and the cuprous hydrate formed is collected on a filter, washed, transferred while still moist to a basin, and treated with hydrochloric acid and potassium chlorate, whereby it is converted into cupric chloride, which may be titrated with stannous chloride (Champion a. Pellet, *loc. cit.*)

P. Lagrange (*ibid.* 1005) prepares a very stable Fehling's solution, not reduced by boiling either alone or with cane-sugar, by dissolving 10 pts. pure cupric tartrate in 400 caustic soda and 500 distilled water, and keeping the solution at the boiling heat for twenty-four hours, renewing the water as it evaporates. The cupric tartrate is prepared either by decomposing the sulphate with normal sodium tartrate, or by dissolving recently precipitated and well-washed cupric hydrate in the required quantity of sodium tartrate. According to Missaghi (*loc. cit.*) the only way of preserving this test-liquid from alteration is to keep it in sealed vessels.

B. With Mercuric Iodide.—This method is adopted by R. Sachse (*Dingl. pol. J.* ccxxi. 570; *Jahresb. f. Chem.* 1877, 1087). The reagent is prepared by dissolving 18 g. pure mercuric iodide and 28 g. potassium iodide in water, adding 80 g. potassium hydroxide, and diluting to a litre. The reaction is complete when a drop of the mixture no longer produces a brown precipitate in an alkaline solution of stannous oxide. 40 c.c. of the test-solution contain 0.72 g. mercuric iodide, and are equivalent to 0.1342 g. grape-sugar.

According to Strohmer a. Klauss (*Chem. Centr.* 1877, 713), this method is applicable only to the estimation of dextrose in pure solutions of that substance, not in solutions which also contain saccharose. It may, however, also be applied to the

estimation of invert-sugar, provided that no other kind is present in the liquid. Erythro- and achroo-dextrin (the constituents of commercial dextrin) may be boiled for a quarter of an hour with a Fehling's solution containing only half the quantity of Rochelle salt usually added to it, without producing any alteration in it, so that the estimation of dextrose by means of a copper-solution may be effected in presence of these two bodies, whereas Sachse's method would be inapplicable in such a case. In the valuation of different sorts of starch-sugar also, the results obtained by Sachse's method are too high, whereas Fehling's solution, applied with all the precautions already indicated, gives satisfactory results.

According to Heinrich, on the other hand (*Chem. Centr.* 1879, 409), dextrose and invert-sugar may be correctly determined in the presence of very varying amounts of saccharose by the use of an alkaline solution of mercuric iodide containing a smaller proportion of potash than that directed by Sachse. The test-liquid contains 25 grams potassium iodide, 18 grams mercuric iodide, and 10 grams potassium hydroxide in 1000 c.c. water. For the determination of small quantities of invert-sugar not more than 5 c.c. (preferably 2.5 c.c.) of the standard liquid should be employed, which should be previously titrated against a very dilute sugar-solution prepared by inverting saccharose. If less than 0.1 per cent. invert-sugar be present in the liquid under examination, 2.5 c.c. of a solution prepared by dissolving 10 grams KHO in 1000 c.c. water, should be added to each 2.5 c.c. of the standard solution before titration. The standard potassio-mercuric iodide liquid containing only 10 grams KHO per litre is not affected by ammonium salts.

Levulose, $C^6H^{12}O^6$. According to Krusemann (*Ber.* ix. 1465), the rotatory power of levulose (prepared by heating inulin from cleomepane-root with water under pressure) varies with the time during which the heating has been continued, increasing at first up to a certain point, and afterwards diminishing; thus:

After heating for .	8	16	24	32	40	48	56	64 hrs.
The rot. power was	10° 27'	15° 23'	15° 44'	16°	15° 24'	15° 21'	15° 17'	14° 51'

Levulose dissolved in water, and treated with sodium-amalgam at ordinary temperatures, is converted into mannitol, $C^6H^{14}O^6$. Dextrose undergoes the same transformation (Krusemann, *Ber.* ix. 1465).

Invert-sugar. Fruit-sugar. The mixture of equal parts of dextrose and levulose, known by these names, occurs, together with acid malates and tritacin, in the root of couch-grass (H. Müller, *Arch. Pharm.* [3], ii. 500; iii. 1).

The conversion of saccharose into invert-sugar may be effected in pure solutions by heat; it is favoured by the presence of glucose, provided the saccharose-solution is not at its highest degree of concentration; considerably also by mineral salts, such as nitrate and chloride of potassium, slightly by organic salts. The percentage of saccharose inverted is in general much greater in dilute than in concentrated solution. The glucose of refinery molasses is formed by the action of the substances above mentioned (H. Pellet, *Ann. Chim. Phys.* [5], xiii. 394).

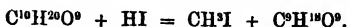
Maumené (*Compt. rend.* lxxx. 1139) finds that invert-sugar varies considerably in composition and properties according to the manner in which it is prepared, and that even when a uniform product is obtained by the use of given quantities of acid and sugar, and maintaining the action at the same temperature and for the same time, it will be variously altered by alkalis, according to the nature and quantity of the alkali used, and especially according to temperature. He regards invert-sugar as a variable mixture of dextrose, levulose, and an optically inactive sugar. This last was obtained by mixing 500 g. white honey with 1 litre of alcohol of 90 per cent. at a gentle heat, and cooling the mass nearly to 0°, whereupon a nearly colourless heavy precipitate having a bulk of 116 c.c. separated, which dissolved almost completely in water, and exhibited no rotatory power, but became slightly dextrogyrate when warmed. Milk of lime added to the cooled solution threw down a lævogyrate sugar, while the solution turned the plane of polarisation to the right.

Invert-sugar is oxidised by nitric acid to oxalic acid, by manganese dioxide and sulphuric acid, and by lead dioxide to formic acid (H. Müller, *Arch. Pharm.* [3], iii. b).

On the Estimation of Invert-sugar by means of a solution of Potassio-mercuric Iodide, see above.

Inosite and Nucite, $C^6H^{12}O^6$. Tanret a. Villiers (*Compt. rend.* lxxxvi. 486) found that inosite from muscular flesh and from green peas is crystallographically identical with nucite obtained from the leaves of the walnut (p. 1421). They also find that inosite is accompanied in plants by a fermentable sugar which reduces Fehling's solution, on which account they consider that inosite may be a product of the transformation of glucose.

Matezite, $C^{10}H^{20}O^8$. This sugar has been found by Aimé Girard (*Compt. rend.* lxxvii. 995) in the caoutchouc of Madagascar, accompanying bornesite and dambonite (vii. 206, 421), which it closely resembles. Matezite is white, crystallisable, easily soluble in water, sparingly in alcohol, from which it separates in groups of crystalline nodules, hard and grating between the teeth. It melts at 181° , and, when cautiously heated, sublimes at 200° – 210° . It is lævogyrate, its rotatory power being 79° . With sulphuric acid, nitric acid, copper-solution, and ferments, it reacts in the same manner as dambonite and bornesite. Heated with fuming hydriodic acid in a sealed tube at 110° , it is resolved into methyl iodide and another sugar, $C^8H^{16}O^6$, called matezodambose:



Matezodambose is sweet, easily crystallisable, more soluble in water than dambose or borneodambose. It is dextrogyrate, with a rotatory power of 6° . It melts at 235° , and behaves to reagents like dambose and borneodambose. The following table exhibits a comparison of the properties of matezite and its analogues, and of the three sugars produced from them by the action of hydriodic acid:

	M. p.	Rot. power		M. p.	Rot. power
Dambonite, $C^8H^{16}O^6$	205°	none	Dambrose, $C^8H^{16}O^6$	212°	none
Bornesite, $C^8H^{16}O^6$	200	+32°	Borneodambose, $C^8H^{16}O^6$	220	none
Matezite, $C^{10}H^{20}O^8$	181	-79°	Matezodambose, $C^8H^{16}O^6$	235	+6°

SULPHACETAMIDE, $CH^3.CS.NH^2$. See THIAMIDES.

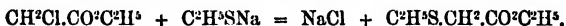
SULPHACROLEIN'SULPHUROUS ACID,



The potassium salt of this acid is formed by adding 1 mol. acrolein by small portions to a well-cooled concentrated solution of 2 mols. sodium-hydrogen sulphite, and is precipitated from the resulting solution by alcohol in the form of a thick mud which gradually solidifies to crystalline nodules. On its products of decomposition, see OXYPHOPANESULPHONIC ACID (p. 1473) (Max Müller, *Ber.* vi. 1441).

SULPHALKYLACETIC ACIDS, $R'.S.CH^2.COOH$ (Clæsson, *Ber.* viii. 120).

Sulphæthylacetic acid, $C^4H^7SO^2 = C^2H^5.S.CH^2.COOH$.—The ethylic ether of this acid, first noticed by Blomstrand (*ibid.* iv. 717), is formed with great evolution of heat, on mixing the alcoholic solutions of ethyl monochloracetate and sodium mercaptide:



On filtering the liquid from the separated sodium chloride and adding water, the ether separates as an oily liquid; and by heating it in sealed tubes with baryta-water, precipitating the excess of baryta with carbonic acid, and decomposing the barium salt with sulphuric acid, the sulphæthylacetic acid is obtained in the form of an uncrystallisable oil. It dissolves readily in alcohol and ether, with moderate facility in water, is partly decomposed when volatilised alone, but may be distilled with vapour of water. Its salts are very easily soluble in water and in alcohol, and do not bear so high a temperature as those of the corresponding phenylated acid (p. 1842). They are oxidised by nitric acid, and yield a brown viscid precipitate with iron salts.

The *potassium salt*, $C^2H^5S.CH^2.CO^2K$, forms deliquescent crystalline crusts slightly soluble in alcohol. The *silver salt*, $C^2H^5SO^2Ag + H^2O$, is a crystalline precipitate which does not give off its water over sulphuric acid. The *barium salt*, $(C^2H^5SO^2)^2Ba$, and the *calcium salt*, $(C^2H^5SO^2)^2Ca$, form radiate groups of needles; the *lead salt* is a viscid mass. The *magnesium salt*, $(C^2H^5SO^2)^2Mg + 3H^2O$, and the *zinc salt*, $(C^2H^5SO^2)^2Zn + 2H^2O$, are crystalline masses. The *cadmium salt*, $(C^2H^5SO^2)^2Cd + H^2O$, is less soluble than the preceding salts, and crystallises in prisms which melt and give off their water at 85° . The *manganese salt* exhibits similar characters. The *cobalt salt*, $(C^2H^5SO^2)^2Co + 2H^2O$, forms small violet-red very soluble prisms. The *nickel salt*, $(C^2H^5SO^2)^2Ni + 2H^2O$, is greenish, and in other respects resembles the cobalt salt. The *copper salt*, $(C^2H^5SO^2)^2Cu + 2H^2O$, forms small shining rhombic plates, which melt at 90° , and decompose with great facility. The *ethylic ether*, $C^2H^5SO^2.C^2H^5$, prepared as above described, is a strongly refracting oil having a powerful odour, a density of 1.0469 at 4° , and boiling at 187° – 189° . It is not acted upon by iodine, but bromine attacks it strongly. Ammonia converts it into *sulphæthylacetamide*, $C^2H^5.S.CH^2.CO.NH^2$, which crystallises in long thin prisms melting at 44° , easily soluble in water and in alcohol, decomposing partially when volatilised. On heating this ether and methyl iodide in molecular proportion in a sealed tube at 120° , and leaving the product to evaporate in a vacuum, yellowish crystals are ob-

tained, consisting of *ethylic diethylsulphiniodacetate*, $(C^2H^3)^2I \equiv S.CH^3.COOC^2H^3$, which, when shaken with silver oxide, yield a strongly alkaline solution.

Sulphamylacetic acid, $C^6H^{11}S.CH^3.CO^2H$, is a thick liquid. Its *ethylic ether* boils at 230° , and has a density of 0.797 at 4° . Its salts, excepting those of its alkalis, are but sparingly soluble. The *zinc* and *cadmium salts* are white precipitates; the *copper salt* crystallises in slender needles. The *lead salt* is very easily fusible.

Sulphphenylacetic acid, $C^6H^5SO^2 = C^6H^5.S.CH^3.COOH$.—The *ethylic ether* of this acid, prepared, like that of sulphothylacetic acid, from ethyl chloracetate and sodium phenylmercaptide, is converted by alcoholic potash into a potassium salt which separates in crystalline spangles, and by decomposing this salt with hydrochloric acid, the free acid is obtained as an oil which soon solidifies to a crystalline mass, and separates from a hot dilute solution on cooling in thin brittle plates. It melts at 43.5° , and resolidifies at 28° ; dissolves in all proportions in alcohol and ether, sparingly in cold water, easily in hot water; the solutions have a strong acid reaction. It is not distillable alone, but volatilises with vapour of water. It is not decomposed by boiling with dilute acid.

The metallic sulphphenylacetates are for the most part slightly soluble in water, insoluble in alcohol; they may all, except the copper salt, be heated to 100° without alteration, but begin to blacken and decompose at 200° . The *potassium salt*, $C^6H^5S.CH^3.CO^2K$, crystallises in thin needles having a silky lustre, moderately soluble in hot water; it is not decomposed either by boiling its solution, or by fusing it with potash. The *sodium salt*, $C^6H^5SO^2Na$, which may be obtained directly by decomposing sodium monochloracetate with an alcoholic solution of sodium phenylmercaptide, forms crusts made up of nodular groups of crystals. The *silver salt*, $C^6H^5SO^2Ag + H^2O$, is a white precipitate. The *barium salt*, $(C^6H^5SO^2)^2Ba$, is a crystalline mass of slender needles moderately soluble in hot water. The *calcium salt*, $(C^6H^5SO^2)^2Ca$, forms groups of oblique tablets. The *lead salt*, $(C^6H^5SO^2)^2Pb$, is an amorphous precipitate which quickly hardens and melts at 60° . The *magnesium salt*, $(C^6H^5SO^2)^2Mg + 3H^2O$, forms shining scales; the *zinc salt*, $(C^6H^5SO^2)^2Mg + 2H^2O$, radiate groups of long silky needles; the *cadmium salt*, $(C^6H^5SO^2)^2Cd + H^2O$, shining scales. The *manganese salt*, $(C^6H^5SO^2)^2Mn + 5H^2O$, is a bulky mass of oblique tables. The *copper salt*, $(C^6H^5SO^2)^2Cu$, is a green amorphous easily alterable precipitate, becoming viscid when exposed in the moist state to the air, and being converted by warming with water into tarry masses consisting of a basic salt. The normal salt dissolves readily in ammonia, the solution when left to evaporate in a vacuum leaving blue prisms. The *cobalt*, *nickel*, *aluminium*, *ferrie*, and *chromic salts* are amorphous precipitates. The *ethylic ether*, $C^6H^5S.CH^3.CO.O C^2H^3$, is a liquid boiling with partial decomposition at 276° – 278° , and having, when pure, a sweetish, aromatic, not unpleasant odour. Sp. gr. = 1.136 at 4° ; 1.1269 at 15° . The *amide*, $C^6H^5S.CH^3.CO.NH^2$ prepared from it, crystallises from alcohol in small plates melting at 104° , easily soluble in alcohol, less soluble in water, very slightly in ether.

Bromosulphphenylacetic acid, $C^6H^4Br.S.CH^3.COOH$.—The *ethylic ether* of this acid is formed, with brisk reaction, on adding bromine to a solution of *ethylic sulphphenyl acetate* in carbon sulphide, and by converting it into the potassium salt with alcoholic potash, and decomposing this salt with hydrochloric acid, the free acid is obtained in shining, sparingly soluble needles which melt at 112° .

Oxidation-products of the Sulphalkylacetic Acids. By acting on a salt of either of the preceding acids with potassium permanganate (not with nitric acid, potassium chromate, &c.), it is possible to oxidise the sulphur to SO or SO^2 , without completely breaking up the molecule. In this way the following acids have been obtained.

Sulphonethylacetic acid, $C^4H^8S^2O^4 = C^2H^5.SO^2.CH^3.COOH$.—This acid, separated from its zinc salt by hydrogen sulphide and concentrated in a vacuum, forms a thick uncrystallisable liquid, which, as well as most of its salts, is very soluble in water. The *potassium salt*, $C^4H^8S^2O^4K$, crystallises from alcohol in small colourless very hygroscopic tablets; the *barium salt*, $(C^4H^8S^2O^4)^2Ba$, in small nodules; the *copper salt*, $(C^4H^8S^2O^4)^2Ca + 2H^2O$, in rather large bluish tablets, which give off their water at 140° . The *zinc salt* and the *silver salt* are moderately soluble; the latter crystallises in small needles. The *lead salt* forms small very soluble tablets.

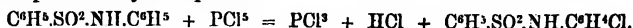
Sulphonphenylacetic acid, $C^6H^5S^2O^4 = C^6H^5.SO^2.CH^3.COOH$, separates on adding an acid to the concentrated solution of its potassium salt, in the first instance as an oil; and on dissolving this in ether and leaving the ether to evaporate, the acid remains in the form of an oil which quickly solidifies. By recrystallisation from water it is obtained in small monoclinic crystals, which melt at 100° , have a very sour taste, and dissolve readily in alcohol and ether. Its salts are more soluble than those of

sulphphenylacetic acid, the potassium and zinc salts being even deliquescent. The *copper salt*, $(C^6H^5SO)^2$, forms small green moderately soluble tablets.

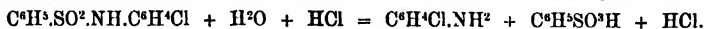
Sulphinephenylacetic acid, $C^6H^5SO^2 = C^6H^5 \cdot SO \cdot CH^2 \cdot COOH$, prepared by oxidising sulphphenylacetic acid with half the quantity of permanganate required for the production of the acid last described, forms colourless crystals melting at 74° . The *copper salt* is a greyish amorphous precipitate.

SULPHAMIDES. The action of phosphorus pentachloride on some of these bodies has been studied by Wallach a. Huth (*Ber.* ix. 424), with results leading to the following general conclusions: (1). Under certain circumstances, phosphorus pentachloride acts like a mixture of chlorine and the trichloride. (2). The production of phosphoretted intermediate products in this reaction appears to be dependent on the particular amidogen-residue attached to the sulpho-group. (3). The oxygen of the group SO^2NH^2 cannot be replaced by chlorine.

Benzenesulphanilide and PCl^5 act upon one another at about 100° in the manner represented by the equation:



The resulting *benzenesulphomonochloranilide* may be obtained by precipitation from the alcoholic solution with water, or better from the benzene solution by precipitation with petroleum-ether, and repeated slow crystallisation from benzene, in splendid crystals melting at 120° – 121° . From ether it crystallises in pyramids. When decomposed by hydrochloric acid it yields monochloraniline melting at 70° :

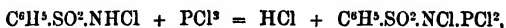


Benzenesulphomonochloranilide may also be prepared synthetically from monochloraniline and benzenesulphochloride. The isomeric compound, *chlorobenzenesulphanilide*, $C^6H^4Cl \cdot SO^2 \cdot NH \cdot C^6H^5$, prepared from parachlorobenzenesulphochloride and aniline, forms needle-shaped crystals melting at 104° .

The action of phosphorus pentachloride on *benzenesulphamide* is in its first stage the same as that which takes place between PCl^5 and benzenesulphotoluide, being represented by the equation:



but the compound $C^6H^5 \cdot SO^2 \cdot NHCl$ is not obtained in the free state, as it is further acted upon by the phosphorus trichloride in the manner represented by the equation:



whereas on benzenesulphochloranilide phosphorus pentachloride exerts scarcely any action.

Wallach a. Huth have confirmed the statements of Limpricht a. von Usler (v. 486) respecting the action of phosphorus pentachloride on *sulphobenzamide*, $C^6H^5 \cdot N^2 \cdot SO^2 = C^6H^5 \cdot (SO^2 \cdot NH^2) \cdot (CONH^2)$, which takes place according to the equation:



the resulting compound forming a yellow syrup, which is further decomposed during distillation, yielding $POCl^3$ and chlorobenzonitril.

On *Mesitylene-sulphamide*, $C^6H^3(CH^3)_3 \cdot SO^2 \cdot NH^2$, and *Parasulphamino-mesitylenic acid*, $C^6H^3(CH^3)_3 \cdot SO^2 \cdot NH^2 \cdot CH^2 \cdot H$, see pp. 1284, 1285.

Sulphamine-isophthalic acids, $C^6H^3NO^2 = C^6H^3(CO^2H)^2(SO^2 \cdot NH^2)$, are formed by oxidation of sulphaminetoluic acids, $C^6H^3(SO^2 \cdot NH^2)(CH^3)(CO^2H)$, and these again by oxidation of xylenesulphamides, $C^6H^3(SO^2 \cdot NH^2)(CH^3)^2$ (q.v.)

SULPHIDES. Rammelsberg (*Ber.* vii. 152) draws attention to the analogy which exists between the dimorphism of iron disulphide and that of the native sulph-arsenides of iron, nickel, and cobalt. There are, in fact, two series of minerals of the general formula $RA^2S(RSbS)$, in which $R = Fe, Ni, Co$, either singly or mixed in various proportions, the minerals of the one series being similar in crystalline form, tendency to hemihedry, and thermoelectric properties to cubical iron pyrites, while those of the other series are similar to marcasite (iii. 402). Since RA^2S may be regarded as $RA^2 + RS^2$, it follows that the metallic arsenides are isomorphous with the disulphides. But the composition of the arsenides of the above metals varies between wide limits, whilst the crystalline form remains the same, as is shown by the following examples: Fe^2As^4 (from Przibram), $FeAs^2$ (Schladming), R^2As^3 (smaltine from Reichelsdorf), RA^2S (Schneeberg), R^2As^3 (Reichelsdorf), $CoAs^3$ (Norway). This would indicate that the arsenides themselves are *isomorphous mixtures*, and, therefore, that though iron and arsenic separately crystallise in different systems, they are yet capable of crys-

tallising isomorphously when allied together. This is further shown by the occurrence of NiAs and NiSb in the hexagonal system, or isomorphous with arsenic and antimony themselves.

These considerations both explain, and receive support from, the almost invariable occurrence of sulphur, in the most variable proportions, in the natural arsenides of iron, &c. Thus Rammelsberg has found gersdorffite (amoibite) to have the formulæ $\text{Ni}^2\text{As}^2\text{S}^2$, $\text{Ni}^2\text{As}^2\text{S}^2$, $\text{Ni}^2\text{As}^2\text{S}^2$, &c. These compounds may be regarded as formed by the union of RS^2 with x molecules of the isomorphous compound R^mAs^n .

Heat of Formation of Metallic Sulphides.—The following determinations of the quantities of heat evolved in the action of hydrogen sulphide on metallic oxides in solution have been made by Berthelot (*Compt. rend.* lxxviii. 1175, 1247).

		kil.-deg.
Na^2O (1 mol. in 1 litres)	+ H^2S (dissolved in 16 litres)	3·85
2NH^3 "	+ H^2S "	3·1
BaO (1 mol. in 10 litres)	+ H^2S "	3·9
MnO (precipitated)	+ H^2S "	5·1
FeO "	+ H^2S "	7·3
ZnO "	+ H^2S "	9·6
PbO "	+ H^2S "	13·3
CuO "	+ H^2S "	15·8
HgO "	+ H^2S "	24·35
Ag^2O "	+ H^2S "	27·9

On comparing these numbers with the heats of neutralisation of the same bases with ether acids, as hydrochloric, nitric, sulphuric, and acetic acid (p. 957), it is found that the heat evolved in the formation of the alkali-metal sulphides in solution is much less than that which is evolved in the formation of the corresponding chlorides, sulphates, acetates, &c.; and accordingly these sulphides are entirely or almost entirely decomposed by hydrochloric, sulphuric, and acetic acid. The thermal determinations showed that the quantity of heat evolved in this reaction is nearly equal to the difference between the heats of neutralisation of the two acids by the alkaline base.

The action of hydrogen sulphide on metallic salts differs considerably according to the nature of the metals and acids, as well as according to the concentration of the solution. Hydrogen sulphide precipitates the dilute solutions of lead, copper, mercury, and silver salts, the reaction being always attended with evolution of heat, which is in accordance with the results of calculation for the solid anhydrous salts. The action of gaseous hydrogen sulphide on the solid acetates of lead and copper gives rise to evolution of heat, and consequently decomposes them. For the chlorides of lead, copper, and mercury on the other hand, negative results are obtained, and accordingly these chlorides are decomposed by hydrogen sulphide only in dilute solution, while on the other hand the corresponding sulphides are decomposed by gaseous hydrogen chloride and even by fuming hydrochloric acid. In like manner solid silver sulphide is decomposed by gaseous hydrogen chloride, bromide, and iodide with evolution of quantities of heat, least with the chloride, greatest with the iodide.

Decomposition in presence of Water.—According to De Clermont a. Frommel (*Compt. rend.* lxxxvii. 230) metallic sulphides in contact with water are first converted into hydrates, which then decompose with separation of hydrogen sulphide, the water in which they are suspended not taking any part in the reaction. On boiling sulphides with water in a vacuum, decomposition was observed to take place at the following temperatures: with arsenious sulphide at 22° ; iron sulphide at 56° ; silver sulphide at 89° ; antimonious sulphide at 95° . The decomposition of arsenious sulphide by boiling with water exhibits certain peculiarities. The evolution of hydrogen sulphide, which is rapid at first, gradually diminishes in consequence of the formation of an oxysulphide of smaller dissociation-tension, the decomposition of which is slower, but nevertheless goes on till the whole of the arsenious sulphide is removed. The decomposition of the sulphide goes on more quickly after addition of crystallised arsenious oxide, than on addition of the vitreous oxide resulting from decomposition of the sulphide. Artificial arsenious sulphide prepared by fusion is but slightly decomposed by water; the native sulphide has a higher tension of dissociation. Native crystallised realgar gave at first a small quantity of hydrogen sulphide, the evolution of which, however, soon ceased, and was probably due to a slight admixture of orpiment, the bisulphide itself not appearing to be decomposed, *Arsenic pentasulphide*, which was never obtained pure, either by precipitation from arsenic acid or from soluble sulpharsenates, yielded as products of decomposition merely arsenious acid and sulphur, never arsenic acid.

On the reduction of the Noble Metals by Metallic Sulphides in Mineral Veins, see METALS (p. 1287).

Action of Acid Potassium Sulphite.—The evolution of hydrogen sulphide observed by Jannettaz (p. 1169) on triturating galena with a solution of this salt, takes place also with other native sulphides, briskly with alabandine, MnS , less strongly in the case of zinc-blende, ZnS , greenockite CdS , and millerite ZnS (Jannettaz, *loc. cit.*)

Action of Ether.—The action of ether on sulphur and various sulphides of iron has been studied by Berthelot (*Compt. rend.* lxxxviii. 890). In every case, on the evaporation of the filtered liquid, crystals of pure sulphur were first deposited, and afterwards a compound containing carbon, hydrogen, and a considerable proportion of combined sulphur. This compound is the result of the chemical action of the sulphur on the solvent, aided by the influence of atmospheric oxygen. The reaction is analogous to that which occurs between free oxygen and hydrocarbons, alcohols, ethers, or aldehydes, by which various ill-defined resinous compounds are produced. In the case of iron sulphides treated with ether, the oxygen of the air unites with the metal, setting free the sulphur, which simultaneously acts on the organic solvent. It is evident, therefore, that the so-called neutral solvents do sometimes act chemically on the substances with which they are placed in contact. Hence statements respecting the pre-existence in meteorites of crystallisable hydrocarbons capable of extraction by organic solvents must be received with great caution.

Oxidation.—Use of Metallic Sulphides as Fuel.—A new application of rapid oxidation by which sulphides may be utilised for fuel has been made by J. Hollway (*Journal of the Society of Arts*, February 1879). When air is blown into molten ferrous sulphide, oxidation proceeds rapidly, in accordance with the equation $FeS + O^2 = FeO + SO^2$, much heat being evolved. This reaction may be utilised by melting iron pyrites with coke in a cupola furnace, transferring the molten ferrous sulphide thus produced to a Bessemer converter, turning on the blast, and from time to time throwing in charges of pyrites and sandstone. In this way, large quantities of pyrites are oxidised without the use of fuel other than that required to heat the blast. A siliceous slag is produced, a quantity of mixed slag and regulus, and a regulus containing nearly the whole of the copper, silver, and gold present in the original pyrites. Preliminary experiments show that the process is of wide application. The special form of plant to be adopted has not yet been determined, the Bessemer converter having been employed only in preliminary trials. The pyrites and sandstone may be thrown into the vessel in lumps.

The experiments hitherto made establish the following points:

When air is blown into a thin stratum of molten ferrous sulphide, the whole of the oxygen is utilised for oxidation. Pyrites being thrown in, as already described, about one-half of the sulphur contained therein is expelled in the free state, with the more volatile metallic sulphides, *e. g.*, lead and arsenic sulphide together present in the pyrites. The plant may be so arranged that this sulphur may be condensed and removed.

The remainder of the sulphur, about 20 per cent. in all, with the exception of that found in the regulus, is principally evolved as sulphur dioxide. The regulus generally contains about 22 per cent. of sulphur; the pyrites about 33 per cent. About 14 per cent. of the escaping gases consists of sulphur dioxide, the remainder being nitrogen. The sulphur dioxide may of course be utilised in the manufacture of sulphuric acid; or it may be condensed in coke towers.

In the ordinary method of burning pyrites, although about 45 per cent. of the sulphur is oxidised, the gases produced contain only about 16 per cent. of sulphur dioxide and 84 per cent. of nitrogen.

If an excess of iron sulphide is always present, copper, silver, gold, nickel, and certain other metals are all concentrated in the regulus. Even if these metals be added in the form of oxide or silicate, it is very probable that these compounds will be converted into sulphides, and that the metals will be concentrated in this form in the regulus. If this be proved experimentally, the process will be suitable for working poor copper ores, slags containing copper, silicates of nickel, &c.

The slag consists chiefly of ferrous ortho-silicate, generally containing traces of copper, small quantities of lead, zinc, &c., and a small percentage of sulphur. The slag being perfectly fused, only small quantities of copper are entangled therein. The small difference between the specific gravity of the slag and that of the regulus (average 4.1 and 4.8 respectively) prevents the complete separation of the latter. It might, however, be possible to add a larger proportion of silica, and so produce a lighter slag.

The exact character of the lining to be used in the furnace remains to be settled:

if sufficient silica be added to produce a slag containing a proportion of silica larger than that required by the formula $\text{SiO}_2 \cdot 2\text{M}^2\text{O}$, the molten slag will exert little or no action on a siliceous lining. In one experiment a peculiar slag was obtained, having the composition $13\text{FeO} \cdot \text{FeS} \cdot 7\text{SiO}_2$, a density of 4.2, a metallic aspect, and crystallised in confused prisms.

Double Sulphides. Sulphur Salts. R. Schneider (*Pogg. Ann.* cxxvi. 460; cxlviii. 625; cxlix. 381; cli. 437; cliii. 588; *Jubelbd.* 1874, 158; *J. pr. Chem.* [2], vii. 214; ix. 209; x. 55).

1. Containing Bivalent Metals. The *potassium-zinc salt*, $\text{K}_2\text{S} \cdot 3\text{ZnS}$, is formed by fusing 1 pt. zinc sulphate, 24 potassium carbonate, and 24 sulphur, at a bright red heat for ten minutes, and remains, on treating the cooled melt with water, in colourless, rhombic laminae, which may be separated by levigation from unaltered zinc sulphide. It is permanent in the air at ordinary temperatures, not even losing its lustre, and appears to undergo only superficial oxidation when heated to redness in an open vessel. It likewise remains unaltered when heated to redness in a stream of hydrogen. It resists the action of water, but is decomposed by mineral acids, even when very dilute, with violent evolution of hydrogen sulphide. When suspended in water holding nitrate of silver or copper in solution, it is converted into the salts Ag_2S , 3ZnS , and $\text{Cu}_2\text{S} \cdot 3\text{ZnS}$ respectively. It is not attacked by mercuric chloride, lead nitrate, or thallous sulphate. The corresponding *sodium salt*, $\text{Na}_2\text{S} \cdot 3\text{ZnS}$, is obtained in the same manner as the potassium salt, but is far inferior to the latter in permanence and in external beauty.

Cadmium sulphide, fused with potassium carbonate and sulphur yields, not a double sulphide, but only the crystallised cadmium sulphide formerly obtained in the same manner by Schüller (*Liebig's Annalen*, lxxxvii. 34); the crystals are hexagonal prisms with pyramidal summits. By fusing 1 pt. cadmium sulphide with 12 pts. dry sodium carbonate and 12 pts. sulphur, the double sulphide $\text{Na}_2\text{S} \cdot 3\text{CdS}$ is produced, but it has not been obtained quite pure, as it is decomposed by water, and dilute alcohol, though it does not decompose the compound, fails to remove a certain quantity of sodium sulphate formed simultaneously with it.

Nickel-potassium Sulphide, $\text{K}_2\text{S} \cdot 3\text{NiS}$, is prepared by fusing 1 pt. crystallised nickel sulphate over a lamp urged by a blast of air, with 9 pts. pure potassium carbonate and 9 pts. sulphur, keeping the mass in red-hot fusion for about ten minutes, and treating the cooled melt with cold de-aerated water. The double sulphide then remains in crystalline laminae, which have a speiss-yellow colour and metallic lustre, and when examined under the microscope appear partly hexagonal, and frequently split in the direction of three lines running from three alternate summits to the centre of the hexagon; partly lozenge-shaped, and then often joined together in rows. This compound alters very quickly in contact with air and water; when ignited in a stream of hydrogen, it gives off only one-fourth of its sulphur. When nickel sulphide is fused with sulphur and *sodium carbonate* (in the proportion 1 : 6 : 6), crystalline laminae are obtained, resembling the potassium compound just described, but of somewhat darker colour, and becoming nearly black-brown when dry.

Cobalt-potassium Sulphide has not been obtained, at least not in the pure state. When metallic cobalt or cobaltous chloride is fused with potassium carbonate and sulphur, a very pure cobalt sesquisulphide, Co^2S_3 , is easily obtained, forming iron-grey crystalline laminae, which appear under the microscope like fissured hexagons, mostly with jagged edges. They are but slightly attacked by hydrochloric acid, or even by aqua regia.

Manganese-potassium Sulphide, $\text{K}_2\text{S} \cdot 3\text{MnS}$.—Völker obtained this compound in dark-red anhydrous laminae, by fusing anhydrous manganous sulphate with potassium carbonate, lamp-black, and sulphur (*Gmelin's Handbook*, English Ed. iv. 237). Schneider, by fusing 1 pt. manganous sulphate with 12 pts. K_2CO_3 and 12 pts. sulphur, obtained, not a double salt, but only manganous sulphide in the form of a green crystalline powder, appearing under the microscope to consist of groups of needles. The *sodium salt*, $\text{Na}_2\text{S} \cdot 3\text{MnS}$, was obtained by Völker (*loc. cit.*) in small shining light-red needles, by a process similar to that employed for the preparation of the potassium salt. Schneider, by fusing together 1 pt. crystallised manganous sulphate, 6 pts. sodium carbonate, and 6 pts. sulphur at a bright-red heat, obtained the compound $\text{Na}_2\text{S} \cdot 2\text{MnS}$, in small thin flesh-coloured shining crystals having a strong tendency to oxidise.

2. Containing Trivalent Metals. *Potassio-indic Sulphide*, $\text{K}_2\text{S} \cdot \text{In}^2\text{S}_3$, is prepared by very intimately triturating 1 pt. indium oxide with 6 pts. pure potassium carbonate and 6 pts. sulphur, and fusing the mixture for eight or ten minutes, first at a moderate heat and finally at a very high temperature. The melt on cooling is found to be filled with numerous light hyacinth-red highly lustrous crystalline

laminae, which remain behind on treating the mass with water, and are obtained quite pure by washing. The laminae are quadratic, mostly very sharply defined, and often joined together in fan-shaped or rosette-shaped groups; translucent with reddish-yellow colour in thin layers. They yield nothing soluble to water, are permanent in the air at ordinary temperatures, and in closed vessels may be heated even to redness without fusion or loss of sulphur, and after cooling appear somewhat darker-coloured than before. When heated in contact with the air, they are slowly converted into a powder which is red-brown white hot, yellow-brown after cooling, and when treated with water, gives up a large quantity of potassium sulphate, but no indium. In hydrogen gas, the double sulphide may be heated to redness without decomposition. It is very easily decomposed by acids, which, if dilute, separate indium sulphide from it, but if concentrated dissolve the whole. It is not attacked by cupric sulphate, thallous sulphate, or lead nitrate, but aqueous silver nitrate converts it, without alteration of form or lustre of the crystals, into black *argenio-indic sulphate*, $\text{Ag}_2\text{S}, \text{In}_2\text{S}_3$.

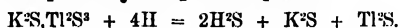
Sodio-indic Sulphide, $\text{Na}_2\text{S}, \text{In}_2\text{S}_3$.—A mixture of 1 pt. indium oxide, 6 pts. sodium carbonate, and 6 pts. sulphur, fused over a blast-lamp, yields a nearly homogeneous red-brown melt; and on treating this with cold distilled water, a clear yellow-brown solution is obtained, which, however, soon becomes turbid, and deposits a large quantity of a dirty-white, somewhat bulky flocculent powder, not unlike freshly-precipitated zinc sulphide. This powder, after washing and drying, has the composition $\text{Na}_2\text{S}, \text{In}_2\text{S}_3 + 2\text{H}_2\text{O}$, and at a somewhat higher temperature is easily converted into the anhydrous compound.

The white precipitate formed by ammonium sulphide in solutions of indium sulphide containing tartaric acid and supersaturated with ammonia, is, according to Schneider, not indium hydrosulphide, as commonly supposed, but ammonium-indium sulphide.

Thallosio-thallic Sulphide, $\text{Ti}^6\text{S}^7 = \text{Ti}_2\text{S}_3, 2\text{TiS}_2$.—When an intimate mixture of 1 pt. thallous sulphate, 6 dry sodium carbonate, and 6 sulphur is fused over a blast-lamp, a melt is obtained, appearing reddish-brown and quite homogeneous when cold, but converted by prolonged treatment with water into a yellow solution free from thallium, and a yellow powder which gradually changes to a network of bulky flocks, and when continuously washed with water, yields up all its sodium sulphide, leaving a residue of thallosiothallic sulphide, probably formed from sodio-thallosiothallic sulphide, $\text{Na} \left\{ \text{S}, \text{Ti}_2\text{S}_3 \right\}$, produced in the first instance. Thallosio-thallic

sulphide is a dark-brown, amorphous, lustreless powder, permanent in the air at ordinary temperatures. When heated in a close vessel, it melts at first without loss of sulphur, and solidifies to a crystalline mass on cooling. When more strongly heated, best in a stream of hydrogen, it gives off sulphur, and is reduced to the monosulphide Ti_2S . Dilute mineral acids decompose the compound Ti_2S_3 , with evolution of hydrogen sulphide and separation of sulphur.

Potassio-thallic Sulphide, $\text{K}_2\text{S}, \text{Ti}_2\text{S}_3$, is obtained by melting together 1 pt. thallium sulphide or chloride with 6 pts. potassium carbonate and 6 pts. sulphur, and remains, on treating the melt with water, as a dark cochineal-red crystalline powder, which, when examined with a moderate magnifying power, is seen to be wholly made up of sharply defined yellowish-red square tablets. Sp. gr. = 4.203. Heated in hydrogen gas, it is decomposed, according to the equation,



The double sulphide is permanent in the air, is not altered by water, and melts, when heated in a small test-tube, to a black-brown liquid, which gives off only a trace of sulphur when heated to low redness, and solidifies on cooling to an indistinctly crystalline mass. When heated in the air it suffers partial oxidation. It is quickly decomposed by hydrochloric and by nitric acid, but aqueous ammonia and potash do not act upon it. Solution of silver nitrate colours it steel-blue, the potassium and part of the thallium being at the same time replaced by silver.

Thallium sulphate, fused with sulphur and *sodium carbonate*, yields, not the corresponding sodium-compound, but an unstable substance containing only thallium and sulphur, and apparently in the ratio of 4 at. Tl to 5 at. S.

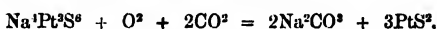
3. Containing Quadivalent Metals. *Tetraplatinous Sulphostannate*. $\text{Pt}_4\text{SnS}_6 = 4\text{PtS}, \text{SnS}_2$, is obtained, as chief product, when 4 pts. of sodio-hypoplatinous stannate, $\text{Pt}_4\text{O}, \text{Na}_2\text{O}, 2\text{SnO}_2$ (vi. 1097), are fused with 6 pts. sodium carbonate and about 8 pts. sulphur, and must be subjected to careful and prolonged levigation to free it from sodioplalinous sulphostannate, $\text{Na}_2\text{S}, 3\text{PtS}, \text{SnS}_2$, formed at the same time as a secondary product. Tetraplatinous sulphostannate is a blackish-grey crystalline

powder, appearing under the microscope as a uniform aggregate of small shining needles. It is permanent in the air at ordinary temperatures, but is completely decomposed by strong and prolonged ignition with access of air. It offers great resistance to the action of acids.

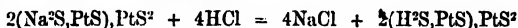
Tetraplatinous Sulphoplatinate, $\text{Pt}^2\text{S}^6 = 4\text{PtS}, \text{PtS}^2$.—This compound (and not platinum sulphide, as stated by Vauquelin), is formed on fusing together equal parts of ammonium platinochloride, sodium carbonate, and sulphur. It crystallises in small needles having a dark steel-grey colour and metallic lustre, and apparently belonging to the orthorhombic system. In the dry state it is not altered by exposure to dry air, but quickly oxidises when moist.

Potassio-platinous Sulphoplatinate, $\text{K}^2\text{Pt}^2\text{S}^6 = \text{K}^2\text{S}, 3\text{PtS}, \text{PtS}^2$, and the corresponding sodium salt, also the *Sulphostannates*, $(\text{K or Na})^2\text{S}, 3\text{PtS}, \text{SnS}^2$, have been already described (vi. 1077).

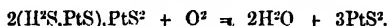
Disodio-platinous Sulphoplatinate, $\text{Na}^4\text{Pt}^2\text{S}^6 = 2(\text{Na}^2\text{S}, \text{PtS}), \text{PtS}^2$, is formed by fusing together spongy platinum, sodium carbonate, and sulphur in the proportion 1 : 6 : 6, and remains, on treating the melt with water, in the form of small thin copper-red needles, which alter somewhat quickly in contact with the air, yielding sodium carbonate and platinum bisulphide :



Hydrochloric acid converts it into the corresponding hydrogen-compound, which is quickly oxidised on exposure to the air :



and



Diargento-platinous Sulphoplatinate, $\text{Ag}^4\text{Pt}^2\text{S}^6$, is obtained by treating the disodium salt with aqueous silver nitrate, in the form of a loose woolly mass of ash-grey thin prismatic crystals which are pseudomorphoses after the sodium-compound. The *thallium salt*, $\text{Tl}^4\text{Pt}^2\text{S}^6$, obtained in like manner with thallous sulphate, also forms pseudomorphoses after the sodium salt, having a steel-grey colour and faint lustre. It is permanent in the air, and when treated with hydrochloric acid, gives up the whole of its thallium without evolution of hydrogen sulphide.

The disodium salt, treated in like manner with *cupric sulphate*, *lead nitrate*, or *mercuric chloride*, yields analogous sulphur-salts; but it is not decomposed by the normal salts of the earth-metals: hence it appears that this salt is decomposed only by the salts of those metals which are precipitated from their neutral solutions by sodium sulphide.

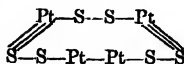
Cuproplatinous Sulphoplatinate, $\text{Cu}^2\text{Pt}^2\text{S}^6 = 2(\text{CuS}, \text{PtS}), \text{PtS}^2$, forms an aggregate of faintly lustrous dark blue-grey needles, which are true pseudomorphs of the disodium salt. They are permanent in the air at ordinary temperatures, and when heated in contact with the air, smoulder away like tinder, giving off sulphur dioxide and trioxide, and leaving a blackish-grey mixture of cupric oxide and metallic platinum. Boiling hydrochloric and nitric acids decompose them partially, abstracting the copper and leaving dark steel-grey needles, and they are not completely decomposed even by boiling aqua regia.

Plumboplatinous Sulphoplatinate, $2(\text{PbS}, \text{PtS}), \text{PtS}^2$, forms a loose aggregate of dark blackish-grey needles, which are permanent in the air at ordinary temperatures, smoulder away with slight decrepitation when heated in the air, giving off sulphur dioxide and leaving a grey mixture of platinum and lead sulphate. This salt is but slightly attacked by hydrochloric acid even at the boiling heat, more strongly by nitric acid, but is not readily decomposed even by aqua regia.

A compound of mercurio-platinous sulphoplatinate with mercuric chloride, agreeing nearly with the formula $2(\text{HgS}, \text{PtS}), \text{PtS}^2 + 2\text{HgCl}^2$, is obtained by the action of a solution of mercuric chloride on disodioplatinous sulphoplatinate. It forms a loose spongy network of thin needles, having a dark ash-grey colour and very little lustre. It is decomposed by aqua regia, but not completely even after long boiling.

Lastly, by treating recently prepared and thoroughly washed disodioplatinous sulphoplatinate immersed in de-aërated water with a dilute solution of sodium-platinochloride, and leaving the resulting black-grey mass at rest for about an hour, merely stirring the platinum solution occasionally, then filtering, pressing the crystals, and drying them out of contact with the air, a compound is obtained which has the composition PtS^3 , but may be regarded as formed from the disodioplatinous salt, by

replacement of the four Na-atoms by a quadrivalent atom of platinum, and represented by the constitutional formula



It forms small, blackish-grey, faintly lustrous, needle-shaped crystals, sometimes partially flattened, and having the form of disodioplatinous sulphoplatinate. When exposed to the air it takes up oxygen, quickly if moist, especially if heated, more slowly in the dry state, and forms sulphuric acid.

On the *Sulphopalladates*, Na_2S , PdS_2 , &c., see vol. vii., p. 889.

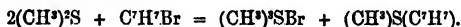
Sulphides of Organic Radicles. The boiling points of several alcoholic sulphides (or alkyl sulphides) have been determined by E. O. Beckman (*J. pr. Chem.* [2], xvii. 439), with the following results:

Sulphides	B. p.	Sulphides	B. p.
Dimethyl	37.1°-37.5°	Ethyl-amyl	159.7°-160.1°
Methyl-ethyl	68°	Di-isobutyl	170.5°
Diethyl	91.9°	Di-isopentyl	213°-214°
Di-isopropyl	120.5°	Ethyl-phenyl	204°

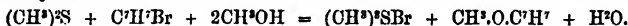
Di-isobutyl sulphoxide, $[(\text{CH}_3)_2\text{CH}.\text{CH}_2]^2\text{SO}$, melts at 68.5°; di-isopentyl sulphoxide, $[(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_2]^2\text{SO}$, at 37°.

SULPHINES. The following sulphine compounds of the fatty series have been prepared and examined by Cahours (*Compt. rend.* lxxx. 1317; lxxxi. 1163; *Ann. Chim. Phys.* [5], x. 13) in continuation of his former researches on these bodies (v. 881).

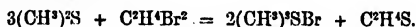
Trimethyl-sulphine bromide, $(\text{CH}_3)_3\text{SBr}$, is formed: 1. By the action of hydrobromic acid on the hydroxide, $(\text{CH}_3)_3\text{SOH}$ (v. 885), also by that of methyl bromide on methyl sulphide; and, together with methyl-benzyl sulphide, $\text{CH}_3.\text{S}.\text{C}^6\text{H}_5$, by heating 2 mols. methyl sulphide with 1 mol. benzyl bromide in a sealed tube at the temperature of boiling water:



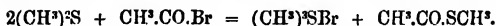
If the mixture is diluted with methyl alcohol, methyl-benzyl oxide is formed instead of the sulphide:



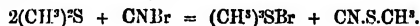
2. Together with ethylene sulphide, by heating ethylene bromide with methyl sulphide in a sealed tube at 100°:



3. In like manner, together with methyl thiocetate, from methyl sulphide and acetyl bromide:



4. Together with methyl thiocyanate, by gradually dropping cyanogen bromide into cooled methyl sulphide, and finally heating the mixture at 100° for an hour or two in a sealed tube:



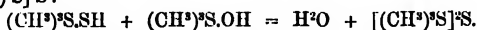
Trimethylsulphine bromide crystallises in prisms easily soluble in water.

Trimethylsulphine iodide, $(\text{CH}_3)_3\text{SI}$, is formed, together with benzyl iodide, by the action of methyl iodide on benzyl sulphide at 100° in a sealed tube; also, like the bromide, by the action of methyl iodide on methyl sulphide. It crystallises from water in large prisms.

Dimethylbenzylsulphine chloride, $(\text{CH}_3)_2\text{S}(\text{C}^6\text{H}_5)\text{Cl}$, is formed by treating the corresponding bromide—which is obtained as a bye-product in the action of methyl sulphide on benzyl bromide—with water and silver oxide, and then with hydrochloric acid. It unites with platonic chloride, forming the compound $[(\text{CH}_3)_2\text{S}(\text{C}^6\text{H}_5)\text{Cl}]^2\text{PtCl}_4$, which crystallises in needles (compare Schöller, p. 322).

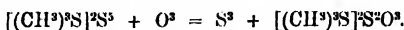
The following salts of trimethylsulphine have been prepared by Blackie a. Crum Brown (*Chem. News*, xxxvii. 130). The *oxalate*, $[(\text{CH}_3)_3\text{S}]^2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$, formed by the action of silver oxalate on trimethylsulphine iodide, crystallises in transparent hygroscopic laminæ, which give off their water of crystallisation at 110°, and decompose at 140°, yielding methyl sulphide and methyl oxalate. The *chromate* and *iodate* prepared in like manner melt at 140° and then explode.

Trimethylsulphine hydrosulphide, $(\text{CH}_3)_3\text{S.SH}$, is formed by treating the hydroxide with hydrogen sulphide: $(\text{CH}_3)_3\text{S.OH} + \text{H}_2\text{S} = \text{H}_2\text{O} + (\text{CH}_3)_3\text{S.SH}$. Heated with an equivalent quantity of the hydroxide, it is converted into *trimethylsulphine sulphide*, $[(\text{CH}_3)_3\text{S}]_2\text{S}$:



The aqueous solution of this last compound, when left over phosphoric anhydride in an atmosphere of coal-gas, does not yield crystals, but is transformed, at a certain degree of concentration, into methyl sulphide, $[(\text{CH}_3)_3\text{S}]_2\text{S} = 3(\text{CH}_3)_2\text{S}$.

Trimethylsulphine sulphide, when treated with sulphur, takes up 4 at. of the latter, forming a polysulphide, $[(\text{CH}_3)_3\text{S}]_2\text{S}_5$, which, when exposed to the air for several days, gives up 3 atoms of sulphur, and is converted into *trimethylsulphinethiosulphate*:



This salt is very hygroscopic, and crystallises in transparent four-sided prisms containing 1 mol. H_2O , which is given off over phosphoric anhydride. It is slightly soluble in alcohol, gives all the reactions of a thiosulphate, and, when cautiously heated to 135° , leaves a residue of methyl sulphide.

On Trimethylsulphine-compounds, see also H. Klinger (*Ber.* x. 1880; *Jahresh. f. Chem.* 1877, 523).

Triethylsulphine bromide, $(\text{C}_2\text{H}_5)_3\text{SBr}$, and the corresponding *chloride*, are formed by treating the hydroxide, $(\text{C}_2\text{H}_5)_3\text{SOH}$ (v. 884), with HBr and HCl respectively. The chloride forms—besides the previously known *platinochloride* (v. 882)—an *aurochloride*, $(\text{C}_2\text{H}_5)_3\text{SCl.AuCl}_3$, which crystallises in long golden-yellow needles, sparingly soluble in cold, moderately soluble in hot water. The *mercurochloride* forms needles having a satiny lustre.

Propyldiethylsulphine iodide, $(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)_2\text{SI}$, is formed, like the corresponding methyl-diethyl compound, by the action of propyl iodide on ethyl sulphide, $\text{C}_2\text{H}_5\text{I} + (\text{C}_2\text{H}_5)_2\text{S} = \text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_2\text{SI}$, the materials being heated together in sealed tubes for several days at 100° – 120° .

Tripropyl- and Tributylsulphine iodides are formed in like manner by direct combination. Their *platinochlorides* are crystalline. Mixed sulphides are also formed by the action of the sulphides of propyl and butyl on the iodides of methyl and ethyl.

The two following series of compounds, containing the isomeric monatomic radicles *diethylmethylsulphine*, $\text{S}(\text{C}_2\text{H}_5)_2\text{CH}_3$, and *ethylmethylethylsulphine*, $\text{S}(\text{C}_2\text{H}_5)(\text{CH}_3)(\text{C}_2\text{H}_5)$, have been prepared by F. Krüger (*J. pr. Chem.* [2], xiv. 195), who attributes the differences in their properties to differences in the four affinities of the sulphur-atom.

(1). *Diethylmethylsulphine-compounds*.—When ethyl sulphide and methyl iodide in molecular proportions are heated with a little water on a water-bath, diethylmethylsulphine iodide is obtained as a reddish-brown syrupy uncrystallisable liquid; and on agitating this liquid with moist silver chloride, the corresponding chloride, $\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{Cl}$, is formed, which dries up in a vacuum to a pale syrup. The *hydroxide*, which was obtained by decomposing the iodide with moist silver oxide, is likewise uncrystallisable, and is a powerful base; the *nitrate* and *sulphate* crystallise in a vacuum in long deliquescent needles; the *oxalate* and *picrate* could not be obtained in crystals.

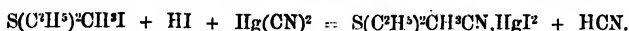
On adding platinic chloride to a solution of the chloride, the *platinochloride*, $[\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{Cl}]_2\text{PtCl}_4$, is obtained as a pale red crystalline powder, which is sparingly soluble in cold water, insoluble in alcohol and ether, and crystallises from hot water in cubes, octohedrons or tetrahedrons, which crumble to a powder on drying. It melts at 214° with decomposition.

The *aurochloride*, $\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{Cl.AuCl}_3$, is readily soluble in alcohol, ether, and hot water, and crystallises in long pale yellow needles, melting with decomposition at 192° .

The *mercurochloride*, $\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)\text{Cl.6HgCl}_2$, is a thick white crystalline precipitate, sparingly soluble in cold water, alcohol, and ether. It crystallises from hot water in prisms resembling rock-crystal, and melting at 198° without decomposition, which takes place only at a higher temperature.

Compound of Diethyl-methyl cyanide with Mercuric iodide, $\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)(\text{CN}).\text{HgI}_2$. When a solution of the crude iodide containing hydriodic acid is mixed with a hot solution of mercuric cyanide, the smell of carbamines and hydrocyanic acid is given off, and a yellow oil is precipitated, which solidifies on cooling, and is insoluble in all solvents. But when cold solutions are mixed, only hydrocyanic acid is evolved, and yellow quadratic crystals separate out, which are insoluble in alcohol, ether, and

carbon sulphide, and very slightly soluble in water, this solution, when evaporated, leaving the compound as an amorphous mass. Its formation is represented by the equation:



It melts at 115° , and decomposes at a slightly higher temperature into mercuric iodide, a carbamino, and a liquid smelling like ethyl sulphide. When treated with hydrogen sulphide in presence of water, it yields mercuric sulphide, which undergoes the known changes of colour, and on continuing the action of the gas, ultimately becomes red, being converted into cinnabar, which, when heated, sublimes as a black mass, yielding again a red powder. Analogous compounds of sulphine-cyanides and mercuric iodide give the same reaction, whereas the double mercuric sulphine-chlorides give black mercuric sulphide.

(2). *Ethylmethyl ethyl sulphine-compounds*.—The iodide, $\text{S}(\text{C}^2\text{H}^5)(\text{CH}^3)(\text{C}^2\text{H}^5)\text{I}$, obtained by heating ethylmethyl sulphide with ethyl iodide and a little water, crystallises in a vacuum in long very deliquescent needles. The chloride does not crystallise; the nitrate and sulphate are as deliquescent as the corresponding salts of diethylmethylsulphine.

The *platinochloride*, $(\text{SC}^2\text{H}^5.\text{CH}^3.\text{C}^2\text{H}^5\text{Cl})_2\text{PtCl}_4$, is a dark red crystalline precipitate insoluble in ether and alcohol, and crystallising from water in apparently monoclinic prisms, which on drying crumble to a rose-coloured powder, and melt with decomposition at 186° . When repeatedly recrystallised or heated for some time with water, it changes into the isomeric diethylmethylsulphine-compound.

$\text{SC}^2\text{H}^5.\text{CH}^3.\text{C}^2\text{H}^5\text{ClAu}, \text{Cl}^3$ is a pale-yellow crystalline powder, readily soluble in hot water, alcohol, and ether, and melting with decomposition at 178° .

$\text{SC}^2\text{H}^5.\text{CH}^3.\text{C}^2\text{H}^5\text{Cl}, 2\text{HgCl}_2$ is a white crystalline precipitate crystallising from hot water in rhombic plates, melting at 112° ; under water it melts below 100° , and does not then crystallise any more.

$\text{SC}^2\text{H}^5.\text{CH}^3.\text{C}^2\text{H}^5\text{CN}, \text{HgI}_2$ is an amber-yellow precipitate consisting of apparently monoclinic prisms; it is insoluble in water, alcohol, and ether, and melts at 98° . When more strongly heated, it yields mercuric iodide, a carbamino, and a sulphide.

On Sulphine-compounds derived from Thiocarbamide, see THIOCARBAMIDE.

SULPHINIC ACIDS, R.SO.OH . *Benzenesulphinic acid*, $\text{C}^6\text{H}^5.\text{SO}^2\text{H}$, is readily obtained by adding zinc-dust to a cooled alcoholic solution of benzene-sulphonic chloride. The zinc salt thus obtained is well washed with water, in which it is almost insoluble, and then decomposed by sodium carbonate, and the resulting solution is concentrated and mixed in the cold with hydrochloric acid, which precipitates the benzenesulphinic acid. In a similar way toluenesulphinic acid may be prepared.

Benzenesulphinic acid is also produced on adding a little water to a few drops of benzenesulphonic chloride and mixing the product with zinc-dust. After some time a brisk reaction sets in, and the zinc salt separates out. More zinc-dust and chloride are now alternately added, care being taken to have the former always in excess. The corresponding *toluene-compound* may be prepared by an analogous process.

The zinc salts of the two acids crystallise from hot water in small nacreous plates, having the composition $(\text{C}^6\text{H}^5\text{SO}^2)_2\text{Zn} + \text{H}_2\text{O}$ and $(\text{C}^7\text{H}^7.\text{CH}^3.\text{SO}^2)_2\text{Zn} + \text{H}_2\text{O}$ (Schiller a. Otto, *Ber.* ix. 1584).

The same method has been applied by Pauly (*Ber.* x. 941) to the preparation of sulphinic acids of the fatty series. *Ethylsulphinic acid of zinc*, $(\text{C}^2\text{H}^5\text{SO}^2)_2\text{Zn} + \text{H}_2\text{O}$, thus prepared, is soluble in hot water, less soluble in alcohol of 90 per cent., from which it crystallises in soft nacreous scales; it agrees in all respects with the salt which Wischlin obtained (*Liebig's Annalen*, cxxxix. 364) by the action of zinc-ethyl on sulphuric anhydride.

Isobutylsulphinic acid of zinc, $(\text{C}^4\text{H}^9\text{SO}^2)_2\text{Zn}$, prepared by the action of zinc-ethyl on isobutylsulphonic chloride, $\text{C}^4\text{H}^9\text{SO}_2\text{Cl}$, forms rather large white nacreous laminae, sparingly soluble in cold, more readily in hot water and alcohol. From alcohol it crystallises anhydrous; from water, apparently with water of crystallisation. It melts with decomposition below 100° . *Sodium isobutylsulphinate* crystallises with difficulty in thin laminae easily soluble in water and in alcohol. The *barium salt* exhibits similar characters. Free isobutylsulphinic acid is a faintly-yellow strongly acid syrup, which dissolves easily in water, and bleaches litmus-paper (Pauly).

SULPHOALDEHYDE, $\text{CH}^3.\text{CHS}$. Syn. with THIOALDEHYDE (*q.v.*)

SULPHOBENZAMIDE, $\text{C}^6\text{H}^5.\text{CS.NH}^2$. Syn. with BENZOTHIAMIDE or THIOBENZAMIDE (*q.v.*)

SULPHOBENZIDE, $\text{C}^6\text{H}^5\text{SO}_2$. See SULPHONES. (p. 1855.)

SULPHOBENZOIC ACID, $C^6H^4 \begin{smallmatrix} CO^2H \\ SO^2H \end{smallmatrix}$ (pp. 293–296). Wiesinger a. Voll-

brecht (*Ber.* x. 1715) have obtained the *meta*- and *para*-modifications of this acid, together with benzoic acid, by the action of alcoholic sulphurous acid on the corresponding diazoimidobenzoic acids.

Sulpho-p-chloro- and *Sulpho-p-bromobenzoic acids*.—These acids and some of their salts have been described by Cöllén and by Röttinger (pp. 295, 296). The following derivatives of the brominated acid are described by Röttinger (*Liebig's Annalen*, xcvi. 13). The crude chlorine-compound prepared by the action of phosphorus pentachloride on the sodium salt in the molecular proportion 1 : 4, is resolved by ether into a sparingly soluble and an easily soluble chlorine-compound. The former, *chlorosulpho-p-bromobenzoic acid*, $C^6H^3Br(SO^2Cl).COOH$, melts with decomposition at 197°, but softens at a lower temperature. It dissolves very sparingly in water and alcohol, somewhat more freely in cold ether, and with moderate facility in hot ether. Alcohol converts it, with liberation of hydrogen chloride, into *ethoxysulpho-p-bromobenzoic acid*, $C^6H^3Br(SO^2.OC^2H^3).COOH$, which crystallises in lustrous plates melting at 84°.

Amidosulpho-p-bromobenzoic acid, $C^6H^3Br(SO^2NH^2).COOH$, prepared by the action of alcoholic ammonia on the monochlorinated acid above mentioned, crystallises in nodular groups of small white needles melting at 229°–230°. It dissolves with difficulty in cold water, easily in boiling water, and with great facility in aqueous ammonia, forming an ammonium salt, $C^6H^3Br(SO^2NH^2).CO^2NH^4$, which loses ammonia on evaporation. When the amido-acid is dissolved in warm baryta-water, small hard glittering needles separate out, consisting of the barium salt.

Ethoxysulpho-p-bromobenzenamide, $C^6H^3Br(SO^2.OC^2H^3).CO.NH^2$, is formed at the same time as the amido-acid by the action of alcoholic ammonia on the dichlorinated compound contained in the crude chloride. Being but sparingly soluble in alcohol and almost insoluble in water, it is easily separated from the acid. It crystallises in long colourless needles, which melt at 128°, and are readily soluble in dilute alkalis; the addition of an acid to this solution produces a crystalline precipitate, consisting of long needles, which melt at 262°, and have the same composition as amidosulphopara-bromobenzoic acid; they appear to consist of *hydrozysulpho-p-bromobenzenamide*, $C^6H^3Br(SO^2OH).CONH^2$.

The action of phosphorus pentachloride on sulpho-p-bromobenzoic acid gives rise also to a dichlorinated compound, viz. *chlorosulpho-p-bromobenzoic chloride*, $C^6H^3Br(SO^2Cl)COCl$; but this compound is easily decomposed by water, the chlorine combined with the CO-group being displaced by OH, producing the monochlorinated acid. That this is the case is conclusively shown by the action of zinc-dust on the alcoholic solution of the monochloride, which gives rise to two compounds: *sulphi parabromobenzoic acid*, $C^6H^3Br(SO^2H).COOH$, which is readily soluble in hot, but only slightly soluble in cold water, and *sulphibromobenzaldehyde*, $C^6H^3Br(SO^2H)COH$, which dissolves in warm water, but is partly thrown down again on boiling. The acid forms small colourless needles, which melt at 238°, with partial decomposition. It is a powerful bibasic acid, and forms crystalline salts. The aldehyde, which may be purified by repeated crystallisation of the barium salt, crystallises in long broad plates, melting at 131°. It is both an aldehyde and a monobasic acid; its barium salt forms large colourless prisms, which rapidly effloresce, and are only slightly soluble in cold water. The compound of the aldehyde with acid sodium sulphite crystallises in long needles melting at 78°. Besides the acid and aldehyde, other compounds, not yet investigated, are produced by the action of zinc on chlorosulpho-p-bromobenzoic acid.

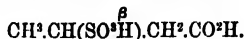
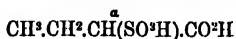
Trisulpho-hydroxybenzoic acid, $C^6H^3S^3O^{12} = C^6H(OH)(SO^2H)^2COOH$, is prepared by heating a solution of 10 grams of benzoic acid in 20 g. sulphuric acid with 5 g. phosphoric anhydride and 20 g. sulphuric anhydride in sealed tubes for five hours. The contents of the tubes are boiled with water to expel sulphur dioxide, and the sulphuric and phosphoric acids are removed by addition of calcium carbonate. To obtain the free acid, basic lead acetate is added to the filtrate, and the precipitated lead salt decomposed by hydrogen sulphide.

Trisulpho-hydroxybenzoic acid is a yellow syrupy hygroscopic liquid, which, when dried at 100°, retains 2 mols. water. Both the acid and its salts produce with a drop of ferric chloride a deep carmine colour, which disappears on addition of sodium carbonate. The *basic lead salt*, $(C^6H^3S^3O^{12})^2Pb^2 + 6H^2O$, forms white opaque needle-shaped crystals which lose their water of crystallisation at 225°. When decomposed by hydrogen sulphide, it is converted into the normal salt, $C^6H^3S^3O^{12}Pb^2 + 8H^2O$. The *basic potassium salt*, $C^6H^3S^3O^{12}K^2 + 2H^2O$, crystallises in monoclinic prisms; the *normal salt*, $C^6H^3S^3O^{12}K^2 + 2H^2O$, separates on adding alcohol to an aqueous solution

of the acid which has been nearly neutralised with potassium carbonate. The *barium salt*, $C^4H^3S^2O^{12}Ba^2$, is decomposed by long-continued heating at 100° , or by boiling with barium carbonate, in the latter case with formation of barium sulphate and barium disulphoxybenzoate, $(C^4H^2S^2O^9)^2Ba + 8H^2O$.

Trisulphoxybenzoic acid appears to be completely decomposed by fusion with potash. On attempting to replace the hydrogen in it by bromine, it splits up into monobromodisulpho- and dibromomonosulphoxybenzoic acids (Kretschy, *Ber.* xi. 858).

SULPHOBUTYRIC ACID, $C^4H^4(SO^3H)(CO^2H)$ (Hemilian, *Ber.* vi. 196, 562; *Liebig's Annalen*, clxxv. 1). Of this acid there are two modifications, viz.:

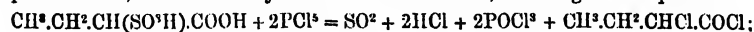


The α -acid is obtained by the action of sulphuric hydroxychloride, $ClSO^2(OH)$, on normal butyric acid. 120 grams of the hydroxychloride are poured upon 100 g. of the acid contained in a retort, and the action, which slackens after a while, is assisted by heating the mixture on an oil-bath finally at 150° . As soon as the evolution of hydrogen chloride ceases, the liquid is diluted with water, the uncombined butyric acid is distilled off, and the strongly coloured residue is boiled for some time with lead oxide, whereby the greater part of the colouring matter is separated; and on filtering and precipitating the lead with hydrogen sulphide, a solution is obtained having only a light yellow colour. This solution is again saturated with lead oxide, the resulting lead salt decomposed with hydrogen sulphide, the free acid then converted into barium salt, and this latter purified by repeated crystallisation. The several mother-liquors thus obtained were perfectly identical, showing that the action of sulphuric hydroxychloride on butyric acid produces only one sulphobutyric acid.

α -Sulphobutyric acid is also formed, together with disulphopropiolic acid, $C^3H^2S^2O^6$, by heating butyramide with fuming sulphuric acid (compare Buckton & Hofmann, v. 569).

α -Sulphobutyric acid, when evaporated in a vacuum over sulphuric acid, remains as an uncrystallisable hygroscopic syrup. Its salts crystallise well. The *barium salt*, $C^4H^4BaSO^3 + 2H^2O$, forms rhombic laminae, gives off its water of crystallisation slowly over sulphuric acid, but remains undecomposed at 200° . 100 pts. water at 16° dissolve 7.11 pts. of the anhydrous salt; aqueous alcohol dissolves only traces. The *calcium salt*, $C^4H^4CaSO^3 + 2H^2O$, separates from the aqueous solution in warty masses; from a solution in alcohol of 50 per cent. mixed with an equal volume of ether in large hemispherical groups of slender needles; this reaction is characteristic of α -sulphobutyric acid. The *silver salt*, $C^4H^4Ag^2SO^3$, is thrown down by alcohol from its aqueous solution as a white amorphous precipitate which soon becomes crystalline. When left in a vacuum and in the dark, it crystallises in large shining quadratic prisms which adhere to the sides of the vessel in stellate groups. The solid salt decomposes at 140° ; the aqueous solution even at ordinary temperatures. The *zinc salt*, $C^4H^4ZnSO^3 + H^2O$, is at first amorphous, but crystallises after some time in large four-sided prisms. The *copper salt*, $C^4H^4CuSO^3 + 4H^2O$, forms a blue-green varnish, or small emerald-green nodules; alcohol separates it from the aqueous solution as a light blue precipitate. The last molecule of water is given off only at a heat above 200° , the salt at the same time undergoing decomposition. The *lead salt*, $C^4H^4PbSO^3 + 2H^2O$, is thrown down by alcohol as an amorphous precipitate. The *magnesium*, *sodium*, and *ammonium salts* are very soluble in water, and crystallise very indistinctly or not at all. The acid heated with alcohol and gaseous hydrogen chloride does not form an ether.

When α -sulphobutyric acid or its barium salt is heated with 2 mols. phosphorus pentachloride, α -chlorobutyric chloride is formed, according to the equation:



and on pouring the distillate—after freeing it from phosphorus oxychloride—into alcohol, ethyl α -chlorobutyrate, $CH^3.CH^2.CHCl.CO.OC^2H^5$, is precipitated in the form of an oil which boils at 154° – 158° . The sulpho-acid does not appear to be converted into a hydroxybutyric acid by fusion with potash. Its barium salt, heated for three hours with fuming sulphuric acid and phosphoric anhydride, yields only traces of disulphopropiolic acid, $C^3H^2S^2O^6$ (v. 569), which, according to Baumstark, is the sole product of the action of sulphuric hydroxychloride on butyric acid (vi. 1069).

β -Sulphobutyric acid, obtained by boiling ethyl β -hydroxybutyrate with ammonium sulphite, is a transparent hygroscopic jelly. Its lead, barium, and calcium salts are thrown down by alcohol from their aqueous solutions in the form of flocculent non-crystalline precipitates. The *barium salt*, dried at 150° , has the composition $C^4H^4SO^3Ba + H^2O$, and gives off its water at 200° (Hemilian).

SULPHOCAMPHYLIC ACID, $C^9H^{16}SO^4$. This acid, discovered by Walter, and originally called *sulphocamphoric acid*, has been further examined by Kachler (*Liebig's Annalen*, clxix. 178), who prepares it by the action of sulphuric acid on camphoric anhydride, exactly according to Walter's directions (v. 489), excepting that, before saturating the diluted and filtered product of the reaction with lead carbonate, he agitates it with ether, which removes unaltered camphoric acid, and an isomeric acid having the property of Wreden's mesocamphoric acid (vii. 235). Sulphocamphylic acid, separated from its lead salt, forms crystalline crusts and druses having the composition $C^9H^{16}SO^4 + 2H^2O$, and giving off their water in a vacuum over sulphuric acid. An acid lead salt, $(C^9H^{16}SO^4)^2Pb + 4H^2O$, was once accidentally obtained from a solution of the normal salt which had been incompletely decomposed by hydrogen sulphide, in nearly colourless well-defined flat prisms. The acid is strongly attacked at a gentle heat by nitric acid of sp. gr. 1.25, with formation of oxalic acid and sulphomelic acid (p. 1860).

The crystals of sulphocamphylic acid, according to measurements by v. Zepharovich (*Wien. Akad. Ber.* lxxiii. [1 Abth.], 1876, 7), are triclinic. $a : b : c = 0.8515 : 1 : 0.7590$. In the first octant, $\alpha = 82^\circ 38'5''$; $\beta = 121^\circ 10'$; $\gamma = 111^\circ 36'$. Observed faces, $\infty P \infty$, $\infty \bar{P} \infty$, $0P$, $3\bar{P} \infty$, $3P$. Measurements only approximate. Cleavage imperfect parallel to $\infty \bar{P} \infty$.

The acid lead salt forms orthorhombic crystals. $a : b : c = 0.7228 : 1 : 0.8080$. Observed forms, $\infty \bar{P} \infty$, $0P$, $\bar{P} \infty$, $3\bar{P} \infty$, $\frac{1}{2}\bar{P} \infty$, P , $\frac{1}{2}P$, $\frac{3}{2}P$. Angle of optic axes for white light = $78^\circ 17'$. Dispersion and double refraction weak.

SULPHO-CARBAMIC ACID, -CARBAMIDE, -CARBONIC ACID, -CYANIC ACID, &c. See the corresponding THIO-COMPOUNDS.*

SULPHONES, R^2SO^2 , and **SULPHOXIDES**, R^2SO . Sulphones are stable compounds, which may be distilled without decomposition, are not reduced by nascent hydrogen (zinc and dilute sulphuric acid) or by hydriodic acid and phosphorus, or attacked by phosphorus pentachloride, whereas the sulphoxides are reduced by nascent hydrogen, and are easily converted into sulphides by the action of phosphorus pentachloride.

Sulphones of the Fatty group may be prepared by oxidising the sulphides and sulphoxides of alcohol-radicles, C^mH^{2m+1} , with potassium permanganate, and extracted from the products with ether (Beckmann, *J. pr. Chem.* [2], xvii. 439).

Dimethyl sulphone, $(CH^3)^2SO^2$, crystallises from alcohol in long thick colourless shining needles melting at 109° . *Methylethyl sulphone*, $(CH^3)(C^2H^5)SO^2$, dissolves easily in water, alcohol, benzene, and chloroform, sparingly in cold ether and carbon sulphide, and crystallises from ether in slender shining needles melting at 36° . *Diethyl sulphone* crystallises from alcohol in rhombic plates. *Diisopropyl sulphone*, $[(CH^3)^2CH]^2SO^2$, forms colourless inodorous crystals which melt at 36° , forming a liquid which often remains for days without solidifying. It dissolves readily in water, alcohol, ether, benzene, chloroform, and carbon sulphide; also in strong nitric, sulphuric, and acetic acids, and is not precipitated from the acid solutions by water. *Diisobutyl sulphone* is a colourless syrupy liquid having a faint but pleasant odour, and a density of 1.0056 at 18° . It boils at 265° , and solidifies in a freezing mixture to a crystalline mass which melts at 17° . It dissolves in 2 pts. water at ordinary temperatures, but is only slightly soluble in hot water; readily in ether, alcohol, benzene, and carbon sulphide; also in strong nitric, sulphuric, and acetic acids, and is reprecipitated therefrom by water. *Diisopentyl- (or diamyl-) sulphone* crystallises in groups of long needles permanent in the air, odourless, but having a sweetish burning taste; melts at 31° , and boils at 295° . It is nearly insoluble in water and aqueous alkalis, but behaves to other solvents like the preceding compound. *Phenylethyl sulphone*, $(C^6H^5)(C^2H^5)SO^2$, produced by oxidation of phenylethyl sulphide, crystallises in thick colourless plates melting at 42° , behaves to solvents much in the same manner as diisopropyl sulphone, excepting that it is precipitated by water from its solutions in acids.

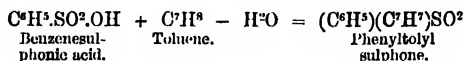
Ethylenediethyl sulphone, $C^2H^4(SO^2.C^2H^5)^2$, formed by the action of permanganate on ethylenediethyl sulphide, crystallises in short, hard, colourless needles, melts at 136.5° , and volatilises without decomposition. It dissolves sparingly in cold, easily in hot water and alcohol, sparingly in ether, benzene, chloroform, and carbon sulphide; easily in strong nitric and sulphuric acids, less easily in hydrochloric, still less in acetic acid.

* The prefix 'thio' is now generally applied to compounds derived from oxy- or hydroxy-compounds by substitution of S for O; the prefix 'sulpho' to bodies containing the group or radicle SO^2H or its analogues, SO^2Cl , SO^2NH^2 , &c.; e.g.:



Aromatic Sulphones. Beckurts u. Otto (*Ber.* xi. 472, 2066) prepare these bodies by the action of aluminium chloride on a mixture of a sulphonic chloride and a hydrocarbon. In this way they have prepared *diphenyl sulphone* or *sulphobenzide*, *ditolyl sulphone* or *sulphotoluide*, *phenyltolyl sulphone*, $[(C^6H^5)(C^6H^4.CH^3)]^2SO^2$; *chlorosulphobenzide*, which melts at 93° , volatilises at a higher temperature, is insoluble in water, sparingly in cold, easily in hot alcohol; and *phenylxylyl sulphone*, $C^6H_5.SO^2.C^6H_4(CH^3)_2$. This last compound, obtained from metaxylene and benzenesulphonic chloride, forms yellowish-white needles, melts at 80° , distils without decomposition, dissolves readily in ether and alcohol, but is insoluble in water.

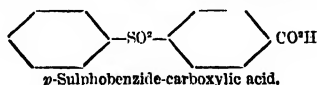
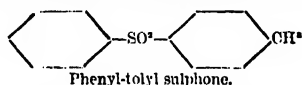
Michael u. Adair (*Ber.* x. 583) prepare aromatic sulphones by heating a mixture of a sulphonic acid and a hydrocarbon in a sealed tube at about 200° with phosphoric anhydride; e.g.:



The product is purified by submitting it to the action, first of a stream of aqueous vapour, then of dilute potash-ley, and lastly of alcohol, the pure sulphone then crystallising from the alcoholic solution. In this manner Michael u. Adair have prepared *ditolyl sulphone*, $(C^6H^4)^2SO^2$, by heating paratoluenesulphonic acid and toluene with phosphoric anhydride for six to eight hours at 150° – 170° , and *phenylnaphthyl sulphone*, $(C^6H^5)(C^{10}H^7)SO^2$ (p. 1357), from benzenesulphonic acid and naphthalene heated for eight or nine hours at 170° – 190° .

Paratolylphenyl sulphone, $C^6H_5.SO^2.C^6H^4(CH^3)$, is prepared in like manner from *p*-toluenesulphonic acid and benzene, or from benzenesulphonic acid and toluene. The product is exhausted successively with water and ether; the residue crystallised from alcohol; and the crystals which separate are freed from coloured impurities by dissolving them in acetic acid, and treating the solution with potassium permanganate. The sulphone thus prepared forms shining white rhombohedral tablets, or when crystallised from water, slender prisms. It melts at 194.5° ; 1.62 pt. of it dissolves at 20° in 100 pts. of absolute alcohol. Ortho- and meta-compounds are not formed simultaneously with the para-compound.

Paratolyl-phenyl sulphone is reduced by nascent hydrogen and by hydriodic acid and phosphorus to the corresponding sulphide. When treated in acetic acid solution with potassium permanganate it is converted into *p-sulphobenzidecarboxylic acid*



This acid crystallises from alcohol in small prisms melting above 300° ; it dissolves sparingly in water, benzene, and glacial acetic acid, easily in nitrobenzene, and forms a flocculent silver salt, $C^6H_5.SO^2.C^6H^4.CO^2Ag$, very sensitive to light. The lead and copper salts are flocculent precipitates.

Ditolylsulphone or *Sulphotoluide*, $(C^6H^4.CH^3)^2SO^2$ (from paratoluenesulphonic acid and toluene), is converted by oxidation into *sulphobenzide-dicarboxylic acid*, $(C^6H^4.CO^2H)^2SO^2$, which very much resembles the monocarboxylic acid, and likewise melts at a temperature above 300° .

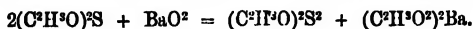
Sulphobenzide-disulphonic acid, $C^6H_5.SO^2.C^6H^4.SO^2.OH$, is formed, together with a small quantity of benzenesulphonic chloride, by heating sulphobenzide with sulphuric hydroxychloride at 120° , and may be extracted from the product by solution in water. Its barium and sodium salts are crystallisable, and have the normal composition Otto u. Knoll, *Ber.* xi. 2075).

On *Hydroxysulphobenzide* (Oxysulphobenzide), $(C^6H^4OH)^2SO^2$, and its derivatives, see pp. 1474–1477.

Sulphoxides, R^2SO . These bodies, and not sulphones, are formed by the action of strong nitric acid on the sulphides. They combine, at ordinary temperatures, with strong nitric acid, forming compounds which contain 1 mol. of the sulphoxide to 1 mol. NO^2H , and are easily decomposed by water. Beckmann has obtained the sulphoxides of diethyl, disobutyl, and ethylenediethyl in the form of viscid syrups. *Disopentylsulphoxide*, heated at 156° with nitric acid of sp. gr. 1.5, is partly converted into isopentylsulphonic acid.

Beckmann has also studied the products obtained by the action of permanganates on sulphides containing an acid-residue and an alcohol-residue. *Acetyl ethyl sulphide* (ethyl thiacetate) is but slightly attacked by potassium permanganate, but a solution of silver permanganate, even when very dilute, is immediately decolorised by it, with formation of acetic and ethylsulphonic acids. *Benzoylisopentyl sulphide* (isopentyl

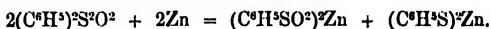
thiobenzoate) is but slightly attacked by the permanganates of potassium and silver, even at the heat of the water-bath; *benzoyl ethyl sulphide* (ethyl thiobenzoate), on the other hand, is attacked by silver permanganate in presence of sulphuric acid, even at ordinary temperatures. *Diacetyl sulphide* (thiacetic anhydride) is oxidised, with incandescence, by barium peroxide; but when the anhydride is diluted with a tenfold quantity of ether, the action begins after some time only, and is attended with only slight evolution of heat, *acetyl persulphide* being formed, probably according to the equation:



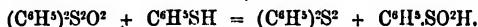
Disulphoxides, $\text{R}^2\text{S}^2\text{O}^2$ (Pauly a. Otto, *Ber.* ix. 1639; x. 2181; xi. 2070). *Diphenyl disulphoxide*, $(\text{C}^6\text{H}^5)^2\text{S}^2\text{O}^2$ (*Benzoldisulfoxid*), which Otto obtained, together with benzenesulphonic acid, by heating benzenesulphinic acid with water (vi. 919), is also produced by the regulated oxidation of phenyl hydrosulphide, $\text{C}^6\text{H}^5\text{SH}$, with nitric acid of sp. gr. 1.3; by the action of strong sulphuric acid or phosphoric anhydride on sodium benzenesulphinate; and by spontaneous decomposition of benzenesulphinic acid, which takes place even in a sealed tube. It melts at 45° , and is resolved by boiling with potash-ley into benzenesulphonic acid, benzenesulphinic acid, and diphenyl disulphide:



Heated in alcoholic solution with zinc-dust, it is quickly and exactly resolved into zinc benzenesulphinate and zinc phenyl mercaptide:



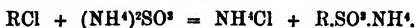
Diphenyl disulphoxide (rather more than 1 mol.) and phenyl hydrosulphide (1 mol.), heated together in alcoholic solution, are exactly resolved into diphenyl disulphide and benzenesulphinic acid:



The same substances heated together directly in the same proportion yield diphenyl-disulphide, benzenesulphonic acid, and decomposition-products of benzenesulphinic acid. Diphenyl disulphoxide is converted by oxidation with potassium permanganate into potassium benzenesulphonate, $(\text{C}^6\text{H}^5)^2\text{S}^2\text{O}^2 + \text{O}^2 + \text{H}^2\text{O} = 2(\text{C}^6\text{H}^5.\text{SO}^2.\text{OH})$.

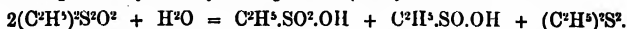
The reactions of *tolyl disulphoxide* are analogous to those of the phenyl-compound.

SULPHONIC ACIDS, $\text{R}.\text{SO}^2.\text{OH}$ (R denoting an organic radicle). A general method of preparing these acids is given by Hemilian (*Liebig's Annalen*, clxviii. 145). It consists in boiling the corresponding chloro- or iodo-compounds with an aqueous solution of normal ammonium sulphite (1 pt. to 2 pts. water), the reaction taking place according to the equation:



By diluting the product with water, boiling it with lead oxide as long as ammonia continues to escape, filtering from the resulting chloride or iodide of lead, and decomposing the filtrate with hydrogen sulphide, the sulphonic acid is obtained in the free state.

(1). **Sulphonic Acids of the Fatty Series.** *Ethylsulphonic acid*, $\text{C}^2\text{H}^5.\text{SO}^2.\text{OH}$, is formed, together with ethylsulphinic acid and ethyl disulphide, by the action of potash-ley on ethyl disulphoxide (Pauly a. Otto, *Ber.* xi. 2073):



An *ethylene-disulphonic acid*, $\text{C}^2\text{H}^4(\text{SO}^2\text{H})^2$, isomeric with disulphetholic acid (v. 566), is formed, together with sulphuric and acetic acids, by oxidising thialdine, $\text{C}^6\text{H}^{11}\text{NS}^2$ (v. 772), with potassium permanganate. It is a syrupy liquid. The same disulphonic acid appears to be formed by oxidation of thioaldehyde (Guareschi, *Ber.* xi. 1384, 1692).

On *Amido-ethylsulphonic acid*, $\text{C}^2\text{H}^4(\text{NH}^2).\text{SO}^2\text{H}$, see TAURINE.

(2). **Of the Aromatic Series.** On *Benzenesulphonic acids*, see pp. 223-259.

Cymenesulphonic acid, $\text{C}^{10}\text{H}^{13}.\text{SO}^2\text{H}$.—According to Paternò (*Gazz. chim. ital.* 1878, 291), the sodium salt of this acid crystallises, not with 5 mols. water, as stated by Jacobsen (*Ber.* xi. 2049), but with only 3 mols.

Pseudocumenol-sulphonic acid, $\text{C}^6\text{H}(\text{CH}^3)^2(\text{OH}).\text{SO}^2\text{H}$, is formed by dissolving pseudocumenol in strong sulphuric acid, and separates from the solution in small shining crystals having the form of cupric sulphate; on adding water to the solution, a crystalline pulp is precipitated, consisting of the hydrated acid. The potassium and zinc salts crystallise in rather long elongated laminæ; the copper salt

in indistinctly crystalline nodules. The *sodium salt* forms easily soluble rectangular tablets; the *barium salt*, thin rhombic tablets, soluble in 20 pts. water at 7°; the slightly soluble *silver salt* consists of rectangular laminæ. The *chloride*, $C^6H^{10}(OH).SO^2.Cl$, forms monoclinic prisms melting at 61°; the corresponding *sulphinic acid*, $C^6H^{10}(OH).SO.OH$, melts at 98° (Reuter a. Radloff, *Ber.* xi. 32).

Phloroglucol-sulphonic acid, $C^6H^2(OH)^2SO^2H$. See PHLOROGLUCOL (p. 1570).

Anthracenedisulphonic acids, $C^{14}H^8(SO^2H)^2$. — Anthracene, treated with sulphuric acid, yields two disulphonic acids which, by fusion with potash, are converted into corresponding dihydroxyanthracenes; and by oxidation of the acetyl-derivatives of these bodies, one of them is converted into chrysazin (p. 108), the other into anthrarufin—a dihydroxyanthraquinone produced also by the action of sulphuric acid on meta-hydroxybenzoic (ordinary oxybenzoic) acid (see ADDENDA) (Liebermann, *Ber.* xi. 1610). To prepare this last-mentioned disulphonic acid, Liebermann a. Böck (*Ber.* xi. 1613) heat 100 pts. anthracene with 300 pts. strong sulphuric acid on a very gently warmed water-bath, till about 20–30 pts. anthracene are dissolved. Several sulpho-acids are thereby produced, but only the lead salt, $C^{14}H^8(SO^2)^2Pb$ (dried at 170°), of the disulphonic acid in question separates from the strongly concentrated solution as a slightly soluble yellow precipitate. The corresponding *sodium salt*, $C^{14}H^8(SO^2Na)^2 + xH^2O$, forms silvery more or less yellow laminæ easily soluble in water, the solution exhibiting a strong blue fluorescence, especially when dilute. The *barium salt* crystallises with 4 mols. water in white nacreous laminæ. The *free acid* forms easily soluble flocks consisting of microscopic needles.

Naphthalene-sulphonic acids, pp. 1353–1355.

Toluene-sulphonic and Xylenc-sulphonic acids, see TOLUENE and XYLENE.

Diazinsulphonic Acids.* This name may be applied to a group of compounds discovered by Griess (*Ber.* xi. 2191), and named by him *Sulphoxybenzenephénols*. They are produced by the action of phenols and their derivatives on diazobenzene-sulphonic acids and other diazo-compounds. Some of them are dye-stuffs, known in commerce as tropeoline, chrysoidine, rocelline, &c.

The positions of the hydroxyl- and sulphonyl-groups in the following compounds with regard to the N^2 -groups may be denoted by figures (as in the naphthalene-derivatives, p. 1375), plain on the right, accented on the left.

i. [4'-4] *Hydroxydiphenyldiazinsulphonic acid*, $C^6H^4(OH).N=N.C^6H^4(SO^2H)$, or $OH \langle \text{---} \rangle N=N \langle \text{---} \rangle SO^2H$. The potassium salt of this acid is obtained by gradually stirring into a solution of phenol in a tenfold quantity of 10 per cent. potash-ley, a quantity of paradiazobenzenesulphonic acid equivalent to the phenol present. The resulting deep yellow-red liquid is left at rest for a short time, then heated and supersaturated with acetic acid, whereupon it yields, after cooling, an abundant crop of light yellow laminæ, consisting of the acid potassium salt of the diazinsulphonic acid. The crystals may be separated from the mother-liquor by filtration, and purified by repeated crystallisation from boiling water with the aid of a small quantity of animal charcoal. The free acid may be separated by mixing a hot concentrated solution of this salt with a very large excess of strong hydrochloric acid, and purified by recrystallisation from boiling water containing a small quantity of hydrochloric acid. It is nearly insoluble in hydrochloric acid and in ether, but dissolves readily in water and alcohol, and crystallises from a concentrated aqueous solution in yellow-red prisms with strong violet surface-shimmer. It decomposes when heated, giving off pungent vapours, and leaving a difficultly combustible cinder. Nitric acid, even when diluted with three or four times its volume of water, decomposes it at the boiling heat, forming oily products, which afterwards solidify to yellow crystals. With tin and hydrochloric acid it yields paramidophenol and sulphanilic acid. With bases it forms acid and neutral salts, most of which crystallise well. The *acid potassium salt*,

* The name 'diazin' has been suggested by Dr. Armstrong for compounds of the type $R'-N=N-R'$, hitherto known as 'azo-compounds,' thus:

Diphenyl-diazin					
(Azobenzene.)					$C^6H^5.N = N.C^6H^5$
Phenyl-naphthyl-diazin	:	:	:	:	$C^6H^5.N = N.C^{10}H^7$
Di-naphthyl-diazin					
(Azonaphthalene.)	:	:	:	:	$C^{10}H^7.N = N.C^{10}H^7$

It has the advantage of indicating the relation of these compounds to the hydrazines, $R'.NH.NH.R'$ (p. 1048). The prefix 'azo' is more appropriately applied to compounds in which a nitrogen-atom simply replaces 2 atoms of hydrogen, e.g. Azomethane (Hydrogen Cyanide or Methenyl-nitril), CHN ; Azo-ethane (Methyl Cyanide or Ethenyl-nitril), C^2H^2N ; Azo-toluene (Phenyl Cyanide or Benzonitril), C^6H^5N .

$C^{12}H^9N^2SO^4K$, prepared as above, or by boiling a concentrated aqueous solution of the acid with potassium chloride, forms thin, yellow, highly lustrous rhombic or six-sided plates, mostly imperfectly developed and easily soluble in hot water. The *acid barium salt*, $(C^{12}H^9N^2SO^4)^2Ba + 5H^2O$, obtained by the action of barium chloride on a hot aqueous solution of the acid, crystallises in reddish-yellow microscopic plates only slightly soluble in water, even at the boiling heat. The *normal barium salt*, $C^{12}H^9N^2SO^4Ba$, is obtained by adding barium chloride to a hot strongly ammoniacal solution of the acid, as an orange-coloured precipitate composed of small nodules, and very slightly soluble in water even at the boiling heat.

ii. [4' - 3] *Hydroxydiphenyldiazinsulphonic acid*, $C^6H^4(OH)N=N.C^6H^3(SO^3H)$, or SO^3H

$OH \text{---} \text{C}_6\text{H}_4 \text{---} N=N \text{---} \text{C}_6\text{H}_3 \text{---} SO_3H$, is formed by the action of the metamidobenzenesulphonic acid prepared from metadiabenzene-sulphonic acid, on an alkaline solution of phenol. It is insoluble in ether, dissolves readily in water and alcohol, and to nearly the same amount whether hot or cold, and crystallises from the aqueous solution by spontaneous evaporation in long narrow pentagonal laminæ having a violet shimmer. By tin and hydrochloric acid, it is reduced to metamidobenzenesulphonic acid and paramidophenol. The *acid potassium salt*, $C^{12}H^9N^2SO^4K$, crystallises in long needles, and is somewhat more soluble in water than the corresponding salt of the preceding compound.

iii. [3 : 4] *Hydroxydiphenyldiazinsulphonic acid*, $C^6H^5.N=N.C^6H^3(SO^3H)(OH)$, is obtained by the action of diazobenzene nitrate on an equivalent quantity of ortho-phenolsulphonic acid in alkaline solution. The free acid dissolves easily in water and in alcohol, but is nearly insoluble in ether. From a cold concentrated aqueous solution, it separates, on addition of strong hydrochloric acid, in thin, rhombic, yellowish-red, shining laminæ, which change on stirring into microscopic needles. By slow evaporation of its aqueous solution it is obtained in large cherry-red rhombic tables or prisms. With tin and hydrochloric acid, it yields aniline, and the amidophenol-sulphonic acid described by Post (vii. 922).

iv. [2' : 4' - 4] *Nitrohydroxydiphenyldiazinsulphonic acid*,

$C^6H^4(OH)(NO^2)N=N.C^6H^4(SO^3H)$, formed from paradiabenzene-sulphonic acid and orthonitrophenol, is slightly soluble in alcohol, and crystallises therefrom either in slender yellow needles or in well-defined rhombic or hexagonal laminæ. It dissolves with moderate facility in hot water, the solution solidifying on cooling to a crystalline pulp. The dry compound detonates strongly when heated.

v. *Dihydroxydiphenyldiazin-p-sulphonic acid*, $C^6H^3(OH)^2N=N.C^6H^4(SO^3H)$, is formed by the action of paradiabenzene-sulphonic acid on a solution of resorcinol in potash, and separates on addition of acetic acid, in the form of a crystalline acid potassium salt. The free acid separated from this salt by strong hydrochloric acid is nearly insoluble in ether, very slightly soluble in alcohol and in cold water, more freely in hot water, and crystallises in acute rhombic laminæ, often elongated into needle-shaped crystals, steel-blue by reflected, ruby-red by transmitted light. It is decomposed by boiling with nitric acid, and when treated with tin and hydrochloric acid, yields sulphanilic acid and amidoresorcinol. It appears to be identical with the dye-stuff called tropæolin O, which Witt obtained by the action of sulphuric acid on resorcinol-diazobenzene. The *acid potassium salt*, $C^{12}H^9N^2SO^4K$, crystallises in reddish-yellow rhombic or six-sided laminæ, sparingly soluble in cold, easily in hot water. Hydrochloric acid precipitates it from its aqueous solution at first without alteration, but a large excess of the strong acid decomposes it. The *acid barium salt*, $(C^{12}H^9N^2SO^4)^2Ba$, crystallises with $4H^2O$.

vi. The corresponding *meta*-compound, $[N=N : SO^3H = 1 : 3]$, crystallises in yellowish-red slender needles which, like the last compound, are insoluble in ether, but slightly soluble in water. With tin and hydrochloric acid it yields metamidobenzenesulphonic acid and amidoresorcinol. The *acid potassium salt* forms hygroscopic needles, sparingly soluble in cold, easily in hot water.

vii. *Methyldihydroxyphenyldiazin-p-sulphonic acid*,

$C^6H^4(CH^3)(OH)^2N=N.C^6H^4(SO^3H)$, prepared from orcinol in the same manner as the preceding compounds from resorcinol, forms small yellowish-red needles, sparingly soluble in hot, very sparingly soluble in cold water. The *acid potassium salt* has the composition $C^{13}H^{11}N^2SO^4K + 2H^2O$.

viii. *Salicylodiphenyldiazin-p-sulphonic acid*, $C^6H^3(CO^2H)(OH)N=N.C^6H^4(SO^3H)$

crystallises in fine golden-yellow needles, insoluble in ether, sparingly soluble in water, more freely in alcohol. The *acid barium salt*, $(C^{10}H^7N^2SO^3)^2Ba$, obtained by the action of barium chloride on a hot solution of the free acid, forms a light yellow precipitate, somewhat gummy at first, but converted by boiling into irregular six-sided laminæ having a strong lustre; very slightly soluble in cold, more freely in hot water.

ix. *Dihydroxyphenylxylyldiazinsulphonic acid*, $C^6H^2(OH)^2N=N.C^8H^5(SO^3H)$, forms yellowish-red slender needles, sparingly soluble in hot, still less soluble in cold water, more easily in alcohol, insoluble in ether.

x. *Hydroxyl- α -Naphthylphenyldiazin-p-sulphonic acid*,

$\alpha-C^{10}H^6(OH)N=N.C^8H^4(SO^3H)$, is formed from α -naphthol and paradiazobenzene-sulphonic acid, and occurs in commerce as *Poirrier's orange*, No. I. The corresponding β -naphthol compound is *Poirrier's orange*, No. II.

xi. *Hydroxyl- β -Naphthylphenyldiazin-m-sulphonic acid*,

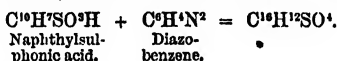
$\beta-C^{10}H^6(OH)N=N.C^8H^4(SO^3H)$, is separated from its orange-coloured aqueous solution by hydrochloric acid in very small blackish-green laminæ, which when pulverised appear gold-green by reflected, violet by transmitted light. It is insoluble in ether, dissolves sparingly in cold water and cold alcohol, more easily in these solvents on warming.

xii. *Hydroxyl- β -Naphthylphenyldiazin-m-sulphonic acid*,

$\beta-C^{10}H^6(OH)N=N.C^8H^4(SO^3H)$, separates on mixing the two solutions as a brown oil, which after some time solidifies in needles. It is slightly soluble in ether, moderately soluble in water and in alcohol. Its powder is gold-green by reflected, red by transmitted light. The *acid barium salt*, $(C^{10}H^{11}N^2SO^3)^2Ba + 5H^2O$, obtained by treating a hot solution of the acid with barium chloride, crystallises in yellowish-red scales having a golden lustre, and sparingly soluble in boiling water.

xiii. *Phenylhydroxyl- α -Naphthyl-diazinsulphonic acid*,

$C^6H^5N=N.\alpha-C^{10}H^6(SO^3H)(OH)$.—The *sodium salt* of this acid is obtained by mixing a solution of sodium- α -naphthylsulphonate with aniline and potassium nitrite:



By dissolving the product in ammonia, precipitating with hydrochloric acid, and repeatedly crystallising it from a hot mixture of alcohol and hydrochloric acid, the free acid is obtained in slender brown-red needles moderately soluble in water, more readily in alcohol, insoluble in ether. It dissolves in alkalis with brown-red colour, changing to deep violet on acidulation. The *sodium salt* is moderately soluble in hot water, less soluble in hot alcohol, insoluble in ether; it is a dye-stuff producing a fine orange-colour inclining to red. At a high temperature it decomposes with strong intumescence. The *silver salt*, $C^6H^{11}N^2SO^3Ag$ (at 100°), crystallises in fine brick-red needles. The *barium salt*, $(C^6H^{11}N^2SO^3)^2Ba$, and the *calcium salt*, are also crystalline precipitates (A. W. Hofmann, *Ber.* x. 1378).

xiv. The corresponding β -naphthyl-compound, obtained by the action of diazobenzene nitrate on an alkaline solution of β -naphtholsulphonic acid, crystallises in red-brown needles having a gold-green surface-shimmer, moderately soluble in water and in alcohol. The *acid barium salt*, $(C^6H^{11}N^2SO^3)^2Ba$, separates on mixing a hot dilute aqueous solution of the acid with barium chloride, in very small nodular groups of yellowish-red microscopic laminæ, which are but very sparingly soluble even in hot water.

xv. *Phenyl-hydroxyl- β -Naphthyl-diazindisulphonic acid*,



is obtained, on mixing the barium salt of Poirrier's orange II. (*supra*) with the exact quantity of sulphuric acid required to decompose it, and evaporating the filtrate, as a yellowish-red crystalline mass, soluble in all proportions in water and in alcohol. Its *acid barium salt*, $C^6H^{10}N^2S^2O^6Ba + 7\frac{1}{2}H^2O$, crystallises in deep orange-red microscopic needles, which dissolve sparingly in hot and very sparingly in cold water.

xvi. *β -Hydroxyldinaphthyl-diazinsulphonic acid*, $\beta C^{10}H^6(OH)N=NC^{10}H^6(SO^3H)$, is produced, as first shown by Caro, by the action of diazonaphthionic acid on β -naphthol. It dissolves very readily in alcohol with blood-red colour, and separates from the boiling-hot solution on addition of hydrochloric acid, in small red-brown needles yielding a blood-red powder, sparingly soluble in cold, more readily in hot water,

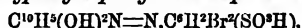
almost insoluble in ether; it is tasteless, and decomposes when heated in a test-tube, leaving a very difficultly combustible cinder. The *acid barium salt*, $(C^9H^{11}N^3SO^4)^2Ba$, is obtained on mixing a moderately strong aqueous solution of the free acid with barium chloride, as a brown-red precipitate composed of microscopic needles.

xvii. *Hydroxydicarboxylphenyl- α -Naphthylhydrazinsulphonic acid*,



formed by the action of diazosulphobenzoic acid on an alkaline solution of α -hydroxynaphthoic acid, crystallises in microscopic needles or laminae having a brown colour with bronze surface-shimmer, sparingly soluble in hot, very sparingly in cold water.

xviii. *Dibromodihydroxyphenylnaphthylhydrazinsulphonic acid*,

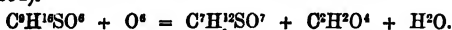


is formed by the action of diazodibromobenzenesulphonic acid on dihydroxynaphthalene. It dissolves with moderate facility in boiling water, forming a yellow solution, from which it is precipitated by hydrochloric acid in violet-brown microscopic needles (Griess).

SULPHOPHENOLIC ACIDS. Syn. with PHENOLSULPHONIC ACIDS (pp. 1538–1540).

SULPHOPHLOGRUCIC ACID. Syn. with PHLOGRUCOLSULPHONIC ACID (p. 1572).

SULPHOPIMELIC ACID, $C^7H^{12}O^7 = C^7H^{11}SO^3H$, is produced, together with oxalic acid, by the action of nitric acid of sp. gr. 1.25, at a gentle heat on sulphocamphyllic acid (p. 1854).



It forms colourless crystals, very soluble in cold water (Kachler, *Liebig's Annalen*, clxix, 178).

SULPHOPROPIONIC ACID, $C^3H^6SO^3$ (A. Kurbatow, *Ber.* vi, 563). The α -modification of this acid, $CH^3.CH(SO^3H).CO^2H$, is formed:—(1). By boiling α -chloropropionyl chloride, $CH^3.CHCl.COCl$, with an aqueous solution of normal ammonium sulphite, in the manner described by Hemilian (p. 1857). (2). By the action of sulphuric hydroxychloride ($1\frac{1}{2}$ pt.) on propionic acid (1 pt.), the mixture being warmed to complete the action, the product then diluted with water, the unaltered propionic acid distilled off, the residue saturated with lead oxide, and the lead salt decomposed by hydrogen sulphide. The acid thus obtained is purified by repeated conversion into lead salt and separation therefrom. The free acid forms a syrup easily soluble in water and in alcohol. The *barium salt*, $C^3H^4BaSO^3 + 2H^2O$, crystallises in colourless shining scales, sparingly soluble in alcohol, more freely in water (7.4 pts. in 100 water). The *calcium salt*, $C^3H^4CaSO^3 + 2H^2O$, is thrown down by alcohol from the aqueous solution as a flocculent precipitate.

The *normal sodium salt* crystallises in deliquescent needles, and the acid salt forms prisms with 3 mol. of water. The *normal potassium salt* is very soluble, and does not crystallise well, and the less soluble acid salt forms needles. The *normal copper* and *silver salts* separate on evaporation in crusts, consisting of microscopic needles. The *zinc salt* is a gummy mass, in which crystals form on standing in the air. The *lead salt* forms glistening crystals.

Sulphophenylpropionic acid, $C^9H^{10}SO^3$, is obtained by reducing the brominated acid with sodium-amalgam. Its *acid barium salt*, $(C^9H^8SO^3)^2Ba + 5H^2O$, forms small tabular triclinic crystals exhibiting the combination ∞P^∞ (predominant) $\infty \bar{P}^\infty .0P$. Axial angles, $\alpha = 87^\circ 26'$; $\beta = 108^\circ 58'$; $\gamma = 78^\circ 6'$.

The crude sodium salt fused with potassium hydroxide yields *meta*-hydroxybenzoic acid; consequently the acid is *meta*-sulphophenylpropionic acid, $C^6.SO^3H.H.C^2H^4(CO^2H).H^2$, and its bromo-derivative is *parabromo-meta*-sulphophenylpropionic acid, $C^6.SO^3H.H.C^2H^4(CO^2H).Br.H^2$.

Bromosulphophenylpropionic acid, $C^9H^8BrSO^3 = C^9H^7Br(SO^3H).CH^2.CH^2.COOH$ (Göring, *Chem. Centr.* 1877. 793, 808). This acid is prepared by adding parabromophenylpropionic acid (p. 1566), in small portions (not exceeding 15 grams), to a threefold quantity of fuming sulphuric acid, care being taken that the temperature of the mixture does not rise above 60° . On diluting the mass with water after twelve hours, a small quantity of bromocinnamic acid separates out; and the filtrate, after due concentration, yields a crystalline deposit of bromosulphophenylpropionic acid, which, when freed from adhering sulphuric acid, crystallises in rhombic plates permanent in the air, having the composition $C^9H^8BrSO^3 + 2\frac{1}{2}H^2O$, and gradually giving off about 2 mol. water over sulphuric acid. The

crystals, according to measurements by Haushofer (*Zeitschr. Kryst.* ii. 91)—who likewise examined the forms of the following salts—are orthorhombic, having the axial ratio $a : b : c = 0.7831 : 1 : 1.3013$, and exhibiting the combination $0P. 3P. P$, tabular according to $0P$, indistinctly cleavable parallel to $0P$. The normal *barium salt* forms a soft mass of felted microscopic needles, only slightly soluble in water even at the boiling heat. The amount of water of crystallisation in this salt (1 or 2 mol.) has not been exactly determined, and the same is true with regard to the following salts. The *acid barium salt*, $(C^6H^4BrSO^3)^2Ba + 8H^2O$, forms triclinic crystals, which quickly effloresce. $a : b : c = 0.4941 : 1 : 0.5046$; $\alpha = 68^\circ 36'$; $\beta = 98^\circ 22'$; $\gamma = 83^\circ 38'$. Observed faces, ∞P_∞ , $\infty P'_\infty$, $0P$, P_∞ , P'_∞ , ∞P , $\infty P'$. Angle $\infty P_\infty : 0P = 78^\circ 25'$; $\infty P_\infty : 0P = 67^\circ 13'$; $\infty P_\infty : \infty P_\infty = 79^\circ 45'$; $\infty P_\infty : P_\infty = 76^\circ 55'$; $0P : P_\infty = 21^\circ 18'$. The brachypinacoid, ∞P_∞ , is vertically striated. No cleavage. The *normal calcium salt*, $C^6H^4BrSO^3Ca + 3H^2O$, forms hard crusts made up of microscopic needles. The *acid calcium salt*, $(C^6H^4BrSO^3)^2Ca + 8H^2O$, is monoclinic. $a : b : c = 0.9774 : 1 : 0.7962$; $\beta = 86^\circ 45'$. Observed faces, ∞P_∞ , R_∞ , ∞P , $\infty P'_\infty$, ∞P_4 . Tabular according to ∞P_∞ , which is mostly vertically striated. Angle $\infty P_\infty : \infty P = 44^\circ 18'$; $\infty P_\infty : R_\infty = 87^\circ 21'$; $R_\infty : R_\infty = 77^\circ 0'$.

SULPHOSALICYLIC ACID, $C^6H^4(OH)(SO^3H)CO^2H$. The two potassium salts of this acid, $C^6H^4K^2SO^3 + 1\frac{1}{2}$ and $2H^2O$, described by Ira Remsen (*vii.* 1125), yield when fused with potash, as sole products, salicylic acid and phenol (*Sill. Am. J.* [3], vi. 284).

SULPHOTOLUIC ACID, $SO^3H.C^6H^4.CO^2H$. See **TOLUIC ACIDS**.

SULPHOTOLUIDE, $(C^6H^4)^2SO^2$. See **SULPHONES** (p. 1855).

SULPHO-UREA. Syn. with **THIOCARBAMIDE** (p. 395).

SULPHO-URETHANE, $NH^2.CO.SCO^2H^2$. Syn. with **ETHYL THIOCARBAMATE** (p. 386).

SULPHUR. *Influence of Gypsum on the Extraction of Sulphur by Distillation.* According to Sestini (*Gazz. chim. ital.* 1874, 29), the saying of the miners in the Romagna, 'that gypsum destroys sulphur,' finds its explanation in the fact that gypsum and sulphur, at the temperature at which the latter distils, act on one another so as to form sulphur dioxide and calcium sulphide, according to the equation $CaSO^4 + 2S = 2SO^2 + CaS$. At the melting point of sulphur this reaction takes place to a slight extent only, and by itself would not occasion any considerable loss of sulphur; but the loss is increased by the circumstance that the expulsion and volatilisation of the crystallisation-water of the gypsum absorbs a quantity of heat which must be supplied by the burning sulphur. When sulphur is distilled under similar conditions over gypsum and over calcium carbonate, the latter gives rise to the formation of a much larger quantity of calcium sulphide than the former.

Physical Properties.—Crystals of sulphur from a mine in Sicily have been found by O. Silvestri (*Gazz.* 1873, 578) to agree exactly in crystalline form and other physical characters with artificially crystallised rhombic sulphur. Sp. gr. = 2.00630 at 26° . Melting point $124-125^\circ$. Solidifying point $96-99.5^\circ$. Specific heat = 0.1776.

On the Expansion-coefficient of Fused Sulphur, as determined by Pisati, see **HEAT** (p. 936).

Gernez (*Compt. rend.* lxxix. 219) finds that it is possible to obtain at pleasure, from the same solution and at the same temperature, either the octohedral or the prismatic modification of sulphur, by dropping into a supersaturated solution of sulphur in benzene or toluene, an octohedral or a prismatic sulphur-crystal; or the two modifications may be obtained simultaneously by dropping in the crystals of the two kinds together.

Further experiments have shown that the octohedral and prismatic modifications may also be produced simultaneously from melted sulphur. Fused sulphur left to cool in a vessel in which it is protected from the dust of the air is easily obtained in the state of superfusion, and may then be made to solidify by contact with a cold body, especially with a fragment of a prismatic sulphur-crystal, or by rubbing two bodies together within the fused mass. The crystals formed under these conditions are always prismatic. If, on the other hand, a fragment of an octohedral sulphur crystal be dropped into the superfused mass, the octohedral modification will be formed, and the solidification will proceed much more slowly. The best way of making this experiment is to melt the sulphur in a U-tube, then leave it to cool, and drop a crystal of octohedral sulphur into one arm of the tube. An octohedral crystal is then immediately seen to form at the surface of the liquid, and to grow downwards till it reaches the lower layers, the solidification being accompanied by a contraction

of volume, evidenced by the sinking of the level of liquid in the other arm by about a seventh of its original height. When one arm of the tube has thus been filled with octohedral crystals, if the surface of the liquid in the other arm be touched with a prismatic sulphur-crystal, this arm of the tube will in a few seconds be completely filled with prismatic crystals of sulphur. The two kinds of crystal are transparent, and at first undistinguishable in appearance; but, on leaving the tube at rest for awhile, the prismatic crystals in contact with the octohedrons become opaque and paler, whilst the octohedral crystals retain their colour and transparency (Gernez, *Compt. rend.* lxxxiii. 217).

According to Barilari (*Gazz.* 1878, 178), the crystals of sulphur which separate from an alcoholic solution of ammonium sulphide at ordinary temperatures are monoclinic.

According to W. R. Hodgkinson (*Chem. News*, xxxiv. 68), the *plastic* modification of sulphur may be obtained in the wet way by passing hydrogen sulphide into a solution of iodine.

On the Isomorphism of Sulphur and Selenium, see Rammelsberg (*Ber.* vii. 669; *Jahresb. f. Chem.* 1874, 206).

Solubility in Acetic Acid.—According to L. Liebermann (*Ber.* x. 866), acetic acid can dissolve a considerable quantity of sulphur. On diluting the solution with water, a precipitate of sulphur-milk is formed; and when it is evaporated under the air-pump, the sulphur remains in the form of long slender prisms.

Direct Oxidation.—According to Pollacci (*Gazz. chim. ital.* 1875, 237), sulphur is directly oxidised by the oxygen of the air. He finds that sulphur, when moistened with water or merely exposed to moist air, is converted after some time into sulphuric acid. Moist flowers of sulphur form in a given time a larger quantity of sulphuric acid than sulphur which has been melted and pulverised, probably because they expose a larger surface to water and air. The crystals of gypsum and sulphur which form in the clefts of San Filippo in Tuscany are often found to be soaked in free sulphuric acid. In the bath-rooms of Aix in Savoy, the limestone walls and the iron plates on the doors and windows are gradually converted into sulphates, and the linen curtains are very quickly destroyed by the action of the free sulphuric acid. All these effects are attributed by Pollacci to the oxidation of hydrogen sulphide.

Relative Affinity of Sulphur and Oxygen for Metals.—O. Schumann (*Liebig's Annalen*, clxxxvii. 286) has endeavoured to determine the relative affinities of sulphur and oxygen for metals from a comparison of the results of experiments on the action: (1) of hydrogen on sulphates; (2) of superheated steam on sulphides; and (3) of hydrogen sulphide on oxides. The substances experimented on were heated in tubes of glass or porcelain, while a current of pure hydrogen, or of steam, or hydrogen sulphide, was passed over them, and the products of the action were then analysed. The results are given in the following table, which shows, also, those previously obtained by other investigators:—

Metal	Action of Hydrogen on the Sulphate	Action of Steam on the Sulphide	Action of Hydrogen sulphide on the Oxide.
Ia.			
Na	—	—	Na ₂ S (Kirscher).
K	K ₂ S (Berzelius).	—	—
Ib.			
Cu	Cu (Arfvedson).	Cu (Regnault).	Cu ₂ S (Schumann).
Ag	Ag (Schumann).	Ag (Regnault) feeble.	Ag ₂ S (Böttger).
IIa.			
Mg	MgO (?)	MgO (Schumann).	Very little MgS (Schumann).
Ca	CaS (Regnault).	CaO + very little CaSO ₄ (Schumann).	4CaS + 3CaO (Schumann).
Sr	SrS (Forster).	SrSO ₄ (Schumann).	2SrS + SrO (Schumann).
	12SrS + SrO (Schumann).		
Ba	BaS (Forster, Schumann).	BaSO ₄ (Regnault, Lauth, Schumann).	BaS (Berzelius).
			3BaS + BaO (Schumann).

Metal	Action of Hydrogen on the Sulphate	Action of Steam on the Sulphide	Action of Hydrogen sulphide on the Oxide
IIb.			
Zn	ZnOS (Arfvedson, Rammelsberg).	ZnO (Regnault).	ZnS (Arfvedson, Schumann).
Cd	CdS + Cd (Schüddler).	CdO ₂ (Regnault, Wackenroder).	CdS (Schumann).
Hg	Hg (Schumann).	Hg (Regnault).	HgS (Schumann).
III.			
Al	Al ² O ³ (Schumann).	Al ² O ³ + a little Al ² (SO ⁴) ³ (Schumann).	A little Al ² S ³ (Schumann).
IV.			
Ti	—	TiO ² (Regnault).	—
Sn	Sn + SnS ² (Arfvedson).	SnO ² (Regnault).	SnS (from SnO) (Schumann).
Pb	Pb + PbS (Arfvedson, Rodwell).	PbS + Pb + PbO (Descotils). PbS + PbSO ⁴ (Pattinson).	SnS ² (from SnO ²). Pb + PbS (Schumann).
V.			
As	—	As ² OS ² (Regnault).	As ² S ² (Schumann).
Sb	Sb ² O ³ + Sb + Sb ² S ³ (Arfvedson).	Sb ² OS ² (Regnault).	Sb ⁴ O ² S ⁴ (from Sb ² O ³). Sb ⁴ OS ³ (from Sb ² O ³) (Schumann).
Bi	Bi (Arfvedson).	Bi (Regnault).	Bi ⁴ S ³ (Schumann).
VI.			
Cr	Cr ² O ³ (Schrötter). Cr ² O ³ + Cr ² S ³ (Traube) 12Cr ² O ³ + Cr ⁴ O ³ S ³ (Schumann).	Cr ² O ³ + Cr ² S ³ (Regnault).	Cr ² S ³ + Cr ² O ² (Schumann).
VII.			
Mn	Mn ² OS (Arfvedson). Fe ² S (from FeO).	Mn ² O ⁴ (Regnault). Fe ² O ⁴ (Regnault).	MnS (Arfvedson). Fe ² O ³ + 1, 2, 3 Fe ² S ³ (Rammelsberg).
Fe	Fe ² S (from Fe ² O ³) (Arfvedson).		Fe ² S ⁶ (Rammelsberg).
Co	Co ² OS (Arfvedson).	CoO (Regnault).	FeS (Sidot). FeS ² (Berzelius). Co ² OS (Schumann). Co ² S ³ (Berzelius). Co ⁴ S ⁵ (Arfvedson). Co ⁴ S ³ (Hjort).
Ni	Ni ² S (Arfvedson).	NiO (Regnault).	NiS (Arf. Schu.)

In group Ia, the experiments are incomplete, owing to the want of vessels which are not attacked by the fused sulphides. There can be little doubt, however, that the sulphides would be converted into sulphates by the action of superheated steam; and since the oxides also yield sulphides with hydrogen sulphide, it follows that the metals of this group have a greater affinity for sulphur than for oxygen.

In group Ib, copper and silver behave exactly alike, and the affinities of sulphur and oxygen for these metals are about equal.

In group IIa, where the metals are arranged in the order of their atomic weights, the affinity for sulphur is seen to increase from magnesium to barium. Magnesium exhibits a greater affinity for oxygen; with calcium, the affinities for sulphur and for oxygen are about equal; whilst strontium and barium display a decidedly greater affinity for sulphur.

In group IIb, the affinities of the metals for sulphur and for oxygen are about

equal. The action of hydrogen on the sulphates shows that the affinities of the metals for both metalloids decrease in the order of the atomic weights, zinc yielding oxy-sulphide and cadmium yielding sulphide, whilst mercury yields only metal.

In group IV, the affinity of the metals is slightly greater for sulphur than for oxygen.

In group VII, manganese and iron exhibit equal affinities for sulphur and for oxygen. Nickel and cobalt show a somewhat greater affinity for sulphur.

The table exhibits a periodic rise and fall in the affinities of the metals for sulphur. In the first group the affinity decreases from potassium to silver. In the second group, it is almost *nil* with magnesium, increases from thence to barium, and decreases to mercury. In the third group, aluminium shows a minimum of affinity for sulphur. In the fourth and fifth groups the affinity for sulphur increases up to arsenic, and then decreases to bismuth. In the sixth group, it is once more at a minimum with chromium, and from thence increases throughout the seventh group.

The general conclusion from these experiments appears to be that the strength of affinity for sulphur in comparison with that for oxygen is greatest in metals of highest atomic volume.

SULPHUR BROMIDES (Hannay, *Chem. Soc. J.* xxvi. 823; xxxiii. 284).

When flowers of sulphur are treated with bromine, about 0.08 per cent. remains undissolved; this portion appears to belong to the prismatic modification, as it remains undissolved also when the flowers of sulphur are treated with carbon sulphide. Pulverised rolled sulphur, on the other hand, is completely dissolved. The vapour which surmounts the mixture of sulphur and bromine exhibits, even at 0°, the characteristic absorption-spectrum of bromine, but on addition of a larger quantity of sulphur this spectrum gradually disappears.

The following are the temperatures at which the spectrum ceases to be visible in a column 0.5 meter long of the vapour standing over different mixtures of sulphur and bromine:

For	S ² Br	S ² Br ²	S ² Br ³	S ² Br ⁴	SBr	S ² Br ⁵	SBr ⁶
Temp.	42°	33°	25°	13°	3°	-7	still visible at -18°

In the distillation of a considerable quantity, the mixture begins to boil at 72°, and the boiling point rises continuously up to that of sulphur, affording therefore no evidence of the formation of a definite compound.

The specific gravities of various mixtures of bromine and sulphur are as follows:

S ² Br	S ² Br	SBr	SBr ²	SBr ³	SBr ⁴
2.293	2.626	2.628	2.820	2.880	2.905

The greatest contraction therefore takes place with the proportion S : Br². On exposure to low temperatures, the mixtures become viscid, but do not solidify even at temperatures at which bromine freezes.

When the fuming liquid S²Br², formed on bringing bromine and sulphur together in the ratio 80 : 32, is exposed to the air in a thin layer, it deposits free sulphur in fine crystals soluble in carbon sulphide, as is also the amorphous sulphur which separates from the liquid on addition of a large quantity of water. Ordinary phosphorus dissolves in the sulphur bromide, with evolution of heat, forming a solution which explodes when an attempt is made to distil it. Amorphous phosphorus does not act on the sulphur bromide. Potassium and sodium in thin plates take fire in contact with it; aluminium powder remains bright in it; antimony powder unites with the bromine without incandescence; arsenic dissolves in it to a colourless fetid liquid. When a small quantity of arsenic is dissolved in SBr², and the liquid is cooled to -18°, dark-red crystals are formed, having the composition AsS²Br³ or possibly AsSBr₂SBr².

From these results, Hannay concludes that when bromine and sulphur are brought together in any proportions whatever, the action between them does not take place in multiple proportions, but is rather an action on the entire mass. If, however, the body SBr² comes in contact at a comparatively low temperature with another with which it can unite, combination between them then takes place in multiple proportions.

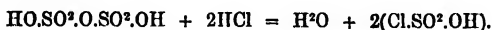
The properties of *sulphur sulphodibromide*, S²Br², have also been investigated by Muir (*Chem. Soc. J.* xxviii. 845). When sulphur and bromine are brought together in the proportion required to produce this compound, they unite, with only slight evolution of heat, which, however, may be increased by agitation. The sulphodibromide begins to distil at 60°, the thermometer then rising slowly to 190°, and by the time it rises to 220°, nearly half of the liquid will have passed over, the residue in the retort being then nearly solid. On rectifying the latter distillate, and collecting apart that which passed over between 190° and 200°, a liquid was obtained consisting

of nearly pure sulphur sulphodibromide, S^2Br^2 (anal. 70.39 p. c. Br; calc. 71.43). When an excess of bromine was added to the sulphodibromide, and carbon dioxide was passed for some time through the liquid at 15° , 50° , and 90° , the residue always exhibited the composition S^2Br^2 . When sulphur was treated with a quantity of bromine larger than that required to form the compound SBr^2 , the whole then placed in a freezing mixture and carbon dioxide passed through it for a considerable time, no definite compound was obtained.

According to Hannay (*Chem. News*, xxxviii. 240), sulphur bromide [$? S^2Br^2$] undergoes complete dissociation at 15° , and the retention of bromine at higher temperatures is due to the passage of the sulphur into the plastic state.

SULPHUR CHLORIDES and OXYCHLORIDES. See viii. 1129–1133.

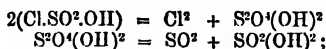
Sulphuric Hydroxychloride, or **Chlorhydrate**, $SO^2(OH)Cl$. This compound may be conveniently prepared by the action of hydrogen chloride on crystallised pyrosulphuric acid, $S^2O^2H^2$:



The acid liquefied by heat is saturated with dry hydrogen chloride, and the hydroxychloride, the formation of which is attended with considerable rise of temperature, is distilled off; it passes over in nearly theoretical quantity as a liquid boiling between 149° and 151° (corr. 150.7° – 152.7°) (Beckurts a. Otto, *Ber.* xi. 2058).

Sulphuric Chloride, SO^2Cl^2 . Williamson observed that the hydroxychloride is resolved by distillation into sulphuric acid and sulphuric chloride, SO^2Cl^2 , and Behrend (*J. pr. Chem.* [2], xv. 23) has founded on this observation a method of preparing the latter compound. He finds that the decomposition takes place readily in a sealed tube at 200° – 210° ; and that on distilling the contents of the tube, purifying the portion which goes over up to 110° by a second distillation on the water-bath, and pouring the whole of this second distillate into a tap-funnel filled with lumps of ice, the ice-cold water instantly decomposes the remaining sulphuric hydroxychloride and the sulphuric anhydride formed in the reaction, whereas the sulphuric chloride is scarcely attacked by it, and sinks to the bottom as a heavy oil. It may be dried with calcium chloride, or better in the exsiccator over phosphoric anhydride, and redistilled at the heat of the water-bath, whereupon it passes over as a colourless, mobile, extremely pungent-smelling liquid, which fumes slightly in the air, boils constantly at 70.5° , has a density of 1.661 at 21° , and vapour-density = 4.751 (calc. 4.677). The yield is about 40 per cent.

According to Beckurts a. Otto (*loc. cit.*), the decomposition of sulphuric hydroxychloride, in the manner above mentioned, is by no means complete, a considerable portion remaining unaltered even after heating for a long time at 170° – 180° . Moreover, chlorine and sulphurous anhydride are amongst the products of the decomposition, and the conversion of the sulphuric hydroxychloride into the chloride appears to take place in such a manner that the hydroxychloride is first resolved into free chlorine and dithionic acid, which latter splits up into sulphurous anhydride and sulphuric acid, according to the equations:



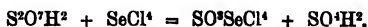
and the chlorine and sulphurous anhydride then unite to form sulphuric chloride.

Action of Sulphuric Chloride on Alcohols.—The products of this reaction are alcoholic sulphuric chlorides, $Cl.SO^2.OR$, analogous to sulphuric hydroxychloride. To prepare them, the alcohol is added by drops to the sulphuric chloride contained in a cooled vessel, and the product is purified by pouring into ice-cold water and drying it over phosphoric anhydride. In this manner have been prepared: *Sulphuric methoxychloride*, $Cl.SO^2.OCH^3$, which is easily decomposed by water; and *sulphuric butoxychloride*, $Cl.SO^2.OC^4H^9$, a pungent-smelling liquid, which is converted gradually at ordinary temperatures, with explosive violence at 80° , into a dark-brown glutinous substance. Benzyl alcohol did not yield a pure sulphochloride (Behrend, *Ber.* ix. 1334).

Sulphuric ethoxychloride, $Cl.SO^2.OC^2H^5$, is formed, together with other products, by the action of sulphuric anhydride on ethyl chloride, also by that of phosphorus pentachloride on potassium ethylsulphate. After drying by means of anhydrous cupric sulphate (calcium chloride decomposes it), it distils almost completely at 80° – 96° under a pressure of 13.5 mm. When ammonia is passed into a solution of this compound in anhydrous ether, a white crystalline mass is formed, which is insoluble in absolute alcohol, and appears by analysis to be a mixture of sal-ammoniac and

sulphuric ethyloxamide, $\text{NH}_2\text{SO}_2\text{OC}_2\text{H}_5$, which could not be separated. With *phenol*, sulphuric ethoxychloride yields two sulphonic acids which have not yet been investigated (T. v. Purgold, *Ber.* vi. 502). With *methyl alcohol*, sulphuric ethoxychloride forms methyl-ethyl sulphate, $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{SO}_4$, a neutral, faintly yellowish liquid, which is also formed by the action of ethyl alcohol on sulphuric ethoxychloride (Behrend).

Sulphur-selenium Oxytetrachloride, $\text{SO}^3\text{SeCl}^4 = \text{ClSO}_2\text{O}.\text{SeCl}^3$, which Rose obtained by the action of sulphuric anhydride on selenium tetrachloride (v. 223), is also produced from the latter: (1). By the action of sulphuric hydroxychloride, $\text{SO}^2\text{Cl}(\text{OH})$. The resulting solution, which has a yellowish to red-brown colour while warm, solidifies on cooling to a crystalline cake, made up of small slender white needles, mostly grouped in radial bundles. (2). By the action of pyrosulphuric acid:



(3). By heating selenium tetrachloride with sulphuric acid:



(4). By heating selenium tetrachloride with pyrosulphuric chloride:

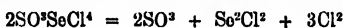


(5). From sulphuryl chloride and selenium oxychloride. At ordinary temperatures these bodies do not act on one another, but mix to a greenish-yellow liquid, which after some time deposits small cubic crystals of selenium chloride; but if the mixture be heated for some hours at 170° – 180° , it solidifies to a crystalline mass of sulphur-selenium oxytetrachloride:



(6). Together with sulphuric acid by heating sulphuryl chloride with selenious anhydride.

Sulphur-selenium oxytetrachloride resembles sulphur oxytetrachloride (vii. 1132) in external appearance, deliquesces with equal rapidity in moist air, but does not decompose spontaneously when excluded from the air, and is not decomposed by heat. It melts at 165° , boils at 183° , is but very slightly attacked by strong sulphuric acid. Its vapour-density at 209° is 3.362, instead of the calculated value 10.426; it therefore undergoes dissociation when heated, probably according to the equation:



(F. Clausnitzer, *Ber.* xi. 2007).

Sulphur-titanium Oxytetrachloride, $\text{SO}^3\text{TiCl}^4 = \text{ClSO}_2\text{O}.\text{TiCl}^3$, is formed, with evolution of hydrogen chloride, when sulphuric hydroxychloride is added by drops to titanium tetrachloride, and remains, on heating the product at 100° , as a yellow amorphous powder, which deliquesces partially in moist air, but may be kept unaltered for a long time apart from the air (Clausnitzer, *loc. cit.*)

SULPHUR, OXIDES and OXYGEN-ACIDS OF. On the Thermic Relations of these Compounds and their Salts, see H&AT (pp. 954–959; 962; 982–989; 996–997).

Hyposulphurous acid, SO^2H^2 .—On the Reaction of this Acid with Aerated Water see OXYGEN (p. 1470).

Sesquioxide, S_2O^3 (R. Weber, *Pogg. Ann.* clvi. 531). The blue substance produced by the action of sulphur on sulphuric oxide (SO^3), or on strongly fuming oil of vitriol, is insoluble in pure sulphuric acid, and may be isolated by the following method. Well-dried flowers of sulphur are gradually added to sulphuric oxide, freed by careful rectification from sulphuric acid, fresh quantities being added only when the previous portions have entered into combination. The sulphur, at the moment of contact with the sulphuric oxide, liquefies to dark-blue drops which do not mix with the oxide, but sink in it and immediately solidify. The operation may be conveniently performed in a test-tube covered with the lid of a small porcelain crucible to protect the contents from the moisture of the air. It is advisable to incline the tube after each addition of sulphur, so that the drops of the resulting compound may come in contact with its surface; they then spread out on the glass, and harden to a thin crust which does not enclose so much of the anhydride as the solidified drops surrounded by the liquid. The tube should be cooled by immersion in water at 12° –

15°, to prevent decomposition by rise of temperature. After about a gram of sulphur has been added, the excess of sulphuric oxide—which is perfectly colourless if the process has been well conducted—is poured off, the last portions of it expelled by very careful evaporation at a temperature not above blood-heat, and the layer of blue substance adhering to the tube is removed with a sharp-edged glass rod. The compound thus prepared forms bluish-green very friable crusts having a structure like that of malachite, and made up of nodular groups of crystals recognisable only with a magnifying glass. It is liquid at the moment of formation, but soon solidifies, and cannot be remelted without decomposition. It decomposes, after a short time, even at ordinary temperatures, and much more quickly when heated, giving off sulphur dioxide, and leaving, if moisture has been excluded, perfectly dry sulphur having a very light yellow colour in consequence of its finely divided state. At low temperatures the decomposition goes on slowly enough to admit of the weighings required for analysis. In moist air the compound quickly absorbs water, and deliquesces to a clear brown liquid, which, on further absorption of moisture, becomes turbid from separation of sulphur. The compound, when dropped into cold water, decomposes instantly with violent hissing, yielding sulphuric and sulphurous acids, together with thiosulphuric acid or a polythionic acid resembling it, and free sulphur, mostly of soft tenacious consistence. With *anhydrous alcohol* or *ether* the blue compound decomposes, with separation of sulphur. Its analysis gave on the average 57·12 per cent. sulphur, agreeing closely with the formula S^2O^3 , which requires 57·14 per cent.

Sulphur sesquioxide dissolves with deep blue colour in a mixture of sulphuric oxide and acid, even if this mixture contains but a small proportion of the latter. Such solutions, if kept in sealed tubes and in a cool place, retain their blue colour for several weeks. Gradually, however, this colour becomes paler, and the solutions acquire a green, afterwards a brown tint, and ultimately a colour like that of common oil of vitriol, sulphurous oxide being at the same time evolved, and sulphur deposited if the quantity of sulphuric oxide present is not very large. Addition of sulphuric acid or of sulphur causes the change of colour to take place immediately. The brown solutions are much more stable than the blue. In an acid containing only 1 mol. SO^3 to 5 mols. SO^2H^2 , the sesquioxide dissolves at once with brown colour. Ordinary sulphuric acid decomposes it immediately, with separation of sulphur.

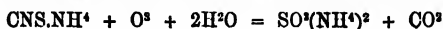
A corresponding *sulphur-selenium compound*, SeSO^3 , is produced by direct combination of selenium with sulphuric oxide. The selenium softens, and is converted into a deep green tarry mass which gradually solidifies; and after decanting the excess of sulphuric oxide, and removing the last portions of it by careful evaporation, the selenium-compound may be scraped out with a sharp-edged glass rod. It has a dingy-green colour in the compact state, yellow in powder. It is much more stable than sulphur sesquioxide, not being decomposed even by gentle heating. At a higher temperature it is resolved, without previous fusion, into sulphur dioxide, selenium dioxide, and selenium. On throwing it into water, a violent reaction takes place, selenium being separated as a coherent mass, and sulphuric, sulphurous, and selenious acids produced. The compound dissolves with deep green colour in sulphuric oxide mixed with sulphuric acid; also without decomposition in strong sulphuric acid, (SO^2H^2), and, on adding a small quantity of water to the solution, it turns brown before completely decomposing. The compound also dissolves with brown colour in sulphuric acid of sp. gr. 1·806 (Weber).

Dioxide, Sulphurous Oxide, or Anhydride, SO^2 . Melsens (*Compt. rend.* lxxvi. 92) prepares this compound, as formerly suggested by Dumas, by the action of sulphur on sulphuric acid. If a glass vessel is used for the purpose, fragments of pumice must be immersed in the acid to ensure the production of a regular current of the gas. With cast-iron vessels it is easy to prepare in this way large quantities of sulphur dioxide.

Pierro (*ibid.* 214) determines the boiling point of the liquid dioxide by placing it in a test-tube of thin glass closed with a cork having two borings, through one of which a thermometer is inserted, while the other affords an escape for the vapours. At ordinary temperatures the sulphurous oxide begins to boil violently, but the boiling soon slackens in consequence of the cold produced by the evaporation; then again becomes violent, once more slackens, and so on. During this fluctuating ebullition, the boiling point scarcely varies by 0·2°. If the tube be wrapped in flannel to prevent the deposition of a film of water on the glass, the limit will be still further narrowed. The boiling point thus determined is about -8°.

Sulphites. *Normal Ammonium Sulphite*, $(\text{NH}^4)^2\text{SO}^3$, is produced by the decomposition of the residues of Laming's masses from gas works, which are used for the preparation of ammonium sulphate. These residues, when left to themselves, become heated, sometimes even to redness, and give off white vapours which may be

condensed in a glass vessel held over the heap, the deposit being found to consist of ammonium sulphite. The masses originally contain—in addition to sulphate of ammonium—considerable quantities of thiocyanate, and the sulphite appears to be formed from this latter salt by oxidation and assumption of water:



(E. Scheitz, *Arch. Pharm.* [3], v. 332).

Sodium-hydrogen Sulphite, SO^2NaH .—This salt is recommended by Th. Schuchardt (*Dingl. pol. J.* ccix. 154) as an antichlor, instead of the thiosulphate. The latter deposits sulphur on the tissues in a very finely divided state, and this sulphur becomes oxidised to sulphuric acid, which gradually destroys the fibre. This inconvenience may be obviated by the use of normal sodium sulphite; but the acid sulphite is preferable, as it acts more strongly and is relatively cheaper.

Sulphite of Palladium and Sodium, $\text{PdSO}^2.3\text{Na}^2\text{SO}^3 + 2\text{H}^2\text{O}$, is formed on mixing a solution of palladium dichloride with sulphurous acid, and gradually adding caustic soda, whereupon a nearly white precipitate is formed, which gradually becomes crystalline, and dissolves in an excess either of sulphurous acid or of soda. When dry, it forms a pale-yellow crystalline powder, which, when heated, first assumes a deeper yellow colour, then decomposes and turns black. Potash and ammonia do not precipitate a solution of palladious chloride mixed with sulphurous acid (Wöhler, *Liebig's Annalen*, clxxiv. 199).

Sulphites of Iridium and Sodium (Seubert, *Ber.* xi. 1761).—In the process of separating iridium from rhodium by means of sodium sulphite, a sodium-iridium sulphite is obtained in the form of a more or less bulky whitish-yellow precipitate. In one of the flasks used for the precipitation, whitish-yellow satiny scales were deposited, having the composition $\text{IrSO}^2.3\text{Na}^2\text{SO}^3 + 10\text{H}^2\text{O}$, and separable for the most part by levigation from the amorphous precipitate formed at the same time. In another flask the precipitate consisted chiefly of broad white needles having the composition $\text{IrH}^2(\text{SO}^3)^2.3\text{Na}^2\text{SO}^3 + 4\text{H}^2\text{O}$. A third salt separated on the sides of the vessel in stellate groups of very slender needles consisting of $\text{IrH}^2(\text{SO}^3)^2.3\text{Na}^2\text{SO}^3 + 10\text{H}^2\text{O}$. All these salts are but slightly soluble in cold water, more abundantly, but not without decomposition, in hot water. They have an acid reaction, and dissolve in acids, with evolution of sulphur dioxide; oxidising bodies change the light colour of their solutions to green, afterwards to blue. With alkalis and alkaline chlorides they yield white precipitates containing the whole of the iridium, and a similar reaction is produced by silver nitrate. When heated, they acquire a darker colour, and give off sulphur dioxide; and at a red heat they leave a skeleton of black iridium and sodium sulphate.

When ammonium chloridate is treated with sulphurous acid, a moss-green powder is obtained, the aqueous solution of which, when strongly concentrated, deposits brown needles of the sesquichloride of iridium and ammonium, $\text{Ir}^2\text{Cl}^2.6\text{NH}^4\text{Cl} + 3\text{H}^2\text{O}$, described by Claus; afterwards, when strongly cooled, beautiful orange-red shining crystals of the salt $\text{IrCl}^2.\text{SO}^2\text{H}^2.4\text{NH}^4\text{Cl}$, which is extremely soluble, but not deliquescent, and has an acid reaction. This compound is an acid capable of decomposing alkaline carbonates, and forming with the alkalis very unstable salts, which lose their power of crystallisation even at the heat of the water-bath, and are separated from their solutions by alcohol in the form of dark-red oils, solidifying, when treated with absolute alcohol, to dark masses. The *potassium salt* has the composition $\text{IrCl}^2.\text{SO}^2\text{K}^2.2\text{NH}^4\text{Cl} + 4\text{H}^2\text{O}$; the *ammonium salt* is $\text{IrCl}^2.\text{SO}^2(\text{NH}^4)^2.2\text{NH}^4\text{Cl} + 4\text{H}^2\text{O}$.

On the compounds of Sulphites with *Pyroracemates*, see PYRORACEMIC ACID (p. 1718).

Sulphur Trioxide, Sulphuric Oxide, or Anhydride, SO^3 . *Formation*.—According to Scheurer-Kestner (*Compt. rend.* lxxx. 1230), the white fumes given off in the combustion of pyrites, consist not of sulphuric acid vapours, but of the anhydride, since they are formed even when the pyrites is perfectly dry. The anhydride is in fact produced by the direct combination of sulphur dioxide with oxygen in presence of red-hot ferric oxide (oxidised pyrites), as Scheurer-Kestner has shown by passing air mixed with sulphur dioxide through a red-hot platinum-tube containing burnt pyrites (*comp.* Wöhler, *Liebig's Annalen*, lxxxi. 255).

Winkler (*Dingl. pol. J.* ccxviii. 128, *Chem. Soc. J.* xxix, 784) has made experiments on the formation of sulphur trioxide by the direct combination of oxygen and sulphur dioxide, platinised asbestos being used as a contact-agent. With a layer of asbestos 30 cm. long and 12 mm. thick, containing 8.5 per cent. platinum, and heated to redness, 100 pts. by weight of sulphur dioxide yielded the following results:—

(a). Mixture of pure SO^2 and pure oxygen	73.3 pts. SO^2
(b). Mixture of pure SO^2 and air	47.4 "
(c). Mixture of air and 4 to 5 vols. per cent. SO^2 obtained by burning sulphur in a current of air	11.5 "

The action of the platinised asbestos (and of other contact-substances) diminishes therefore in proportion as the sulphur dioxide is diluted with indifferent gases.

A mixture of pure sulphur dioxide and oxygen in the required proportions may be obtained from sulphuric acid, which at high temperatures is resolved into SO^2 , oxygen and water.

The apparatus used by Winkler consisted of a wrought-iron tube coated inside and out with a mixture of Chamotte clay and water-glass, this mixture being burnt in, and the tube filled with fragments of porcelain. It was then heated to bright redness in a charcoal fire, and sulphuric acid of 66° was continually dropped into it through a twice-bent funnel-tube. The escaping gases were dried by passing over lumps of pumice drenched with sulphuric acid, and then passed into a long glass tube, horizontal at first, then bent downwards, and having its horizontal part loosely filled with platinised asbestos (containing 8.5 per cent. platinum), whilst the vertical arm dipped into a receiver filled with strong sulphuric acid destined to receive the anhydride formed by the reaction. This receiver was connected with a second, also containing strong sulphuric acid, and the latter with a third containing a solution of sodium carbonate. With this apparatus, 195 grams of sulphuric acid of 66° (= 146.2 g. SO^2) yielded 107.8 g. SO^2 , 22.6 g. SO^2 , 5.6 g. oxygen and 45.8 g. water, while 13.2 g. sulphuric acid remained undecomposed. Consequently 73.7 per cent. of the anhydride contained in the total quantity of sulphuric acid employed, or 78.4 per cent. of the anhydride contained in the sulphuric acid actually decomposed, was obtained in the form of fuming sulphuric or pyrosulphuric acid.

For preparation on the large scale, sulphuric acid of 66° is made to flow in a thin stream into earthenware retorts heated to bright redness, and the products of decomposition are passed, first through a cooling apparatus to condense the water, then through towers filled with coke moistened with strong sulphuric acid, to complete the drying, and finally into tubes of glazed earthenware filled with platinised asbestos, and heated to low redness. From 50 to 103 kg. asbestos, containing 8 kg. platinum, are sufficient for a work of considerable size. The resulting sulphur trioxide is collected in tubes of glazed earthenware, or brought in contact with a shower of sulphuric acid of 66° . The unabsorbed mixture of sulphur dioxide and oxygen is passed into lead chambers.

This process has been patented by Squire & Messel (see further *Dingl. pol. J.* cccxiii. 409).

Properties.—The variation in the melting point of sulphur trioxide according to its mode of solidification, which was attributed by Marignac (v. 569) and Schultz-Sellack (vii. 1135) to the existence of different modifications, has been shown by R. Weber (*Pogg. Ann.* clix. 313) to be due to imperfect purification. Weber has prepared the pure trioxide by repeated distillation, finally in a sealed bent tube. It is at ordinary temperatures a very mobile perfectly colourless liquid, which when slowly cooled solidifies in long transparent crystals resembling those of saltpetre, and quite different from the opaque asbestos-like needles of ordinary sulphuric anhydride; it melts at 14.8° , and boils at 46.2° (bar. 761.6 mm.) Sp. gr. 1.940 at 16° . It may be kept for years without giving any indication of change in its molecular state. By absorption of a small quantity of moisture it is converted into a snow-white, opaque, infusible body, which, if present even in small quantity, diffuses itself through the liquid in flocks, which may easily be made to adhere together in the upper part of a glass tube. This hydrated compound, the proportion of water in which must be very small, is a constituent of the ordinary anhydride, and gives rise to its peculiar properties. Besides this hydrate containing the minimum of water, the cautious addition of ordinary sulphuric acid to the ordinary anhydride gives rise to a liquid product, from which at 8° to 10° spicular crystals separate, having the composition $\text{H}^2\text{S}^2\text{O}^{13}$ or $\text{H}^2\text{O}, 4\text{SO}^2$. In preparing this last hydrate, an excess of common sulphuric acid must be avoided, as even a small quantity of it prevents the separation of these crystals and determines the formation of pyrosulphuric acid, $\text{S}^2\text{O}^7\text{H}^2$, or $\text{H}^2\text{O}, 2\text{SO}^2$.

With reference to these observations of Weber, Marignac (*N. Arch. ph. nat.* lviii. 228) publishes the following results of some now experiments on preparations made twenty-four years ago.

When sulphuric oxide which had been kept in sealed glass tubes was slowly heated in a water-bath, it began to melt on the first day at about 100° ; on the second day it began to become transparent between 50° and 60° ; between 60° and 65° a

partial fusion took place; at 80° it was still only partly fused, and the fusion was not complete till the heat was raised to 95° . In an experiment made on the following day the oxide began to be transparent at 35° – 40° , at 70° the greater part was melted, and at 80° the fusion was complete. The experiment was repeated on the fourth day, the temperature being kept for twenty-four hours between 45° and 50° . After that time three-fourths of the substance was found to be melted, the rest forming a gelatinous mass floating in a liquid. From these observations, Marignac thinks it may be inferred that, even admitting the probability of Weber's supposition as to the solid modification owing its existence to the presence of a hydrated compound, still the gradual alteration of the melting point after repeated fusion can be due only to an isomeric alteration, or to an alteration of the mode of combination of the hydrated compound with the anhydrous oxide. He observes that he formerly examined both the liquid compound and that which fuses only at a higher temperature, and found them both to have the composition SO^3 , so that the amount of water in the solid modification must at all events be extremely small.

With *ethyl chloride*, sulphuric oxide yields sulphuric ethoxychloride, $\text{ClSO}^2\text{OC}^2\text{H}^5$, together with the two isomeric compounds, chlorisethionic acid, $\text{C}^2\text{H}^4\text{ClSO}^2\text{OH}$, and isethionic chloride, $\text{C}^2\text{H}^4(\text{OH})\text{SO}^2\text{Cl}$ (see *ETHYL CHLORIDE*, p. 746).

Sulphuric Acid, $\text{SO}^2\text{H}^2 = \text{SO}^2(\text{OH})^2$. *Manufacture*.—H. A. Smith (*Phil. Mag.* [4], xlii. 121) infers from observations of his own that the best dimensions for the lead chambers are 150 feet long, 20 to 30 broad, and 10 to 12 high. The temperature in the chamber should be kept as nearly as possible at 200° F. ($93\text{--}33^{\circ}$ C.), this temperature being produced and kept up by the vapours which enter the chamber. In starting the operation, the floor of the chamber should be covered with sulphuric acid, not with water.

H. Sprengel has contrived an apparatus by means of which water-spray instead of vapour is introduced into the leaden chambers. A jet of steam is blown through a platinum tuyere into a jet of water, whereby the latter is finely divided. 20 kg. of steam are sufficient to convert 80 kg. of water into spray. By thus dispensing with the evaporation of the water, a considerable saving of fuel is effected. The nitric acid may also be introduced into the chambers in a very similar manner, the Glover tower being thereby reduced to a mere condensing apparatus, and the loss of nitric acid ascribed to it thereby avoided (*Pharm. J. Trans.* [3], vi. 324; *Chem. News*, xxxii. 150).

On Apparatus for the Manufacture of Sulphuric acid, contrived by de Hemptinne, see Bode (*Dingl. pol. J.* ccxvii. 300; ccxiv. 1137; *Jahresb. f. Chem.* 1875, 1053; 1877, 1137). On the roasting of Pyrites, see McCulloch (*Chem. News*, xxvii. 124, 135).

On the Estimation of the Loss of Sulphurous acid in the Lead-chamber process, see Mactear (*Chem. News*, xxxvi. 49).

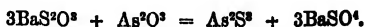
On the Recovery of Nitrogen Oxides in the Manufacture of Sulphuric acid, and the Function of the Glover Tower, see Vorster (*Dingl. pol. J.* ccxiii. 411, 506; *Jahresb. f. Chem.* 1874, 1104; *Chem. Soc. J.* xxvii. 829, 924; and Lunge, *Ber.* x. 1432; *Dingl. pol. J.* 225; *Jahresb.* 1877, 1139; *Chem. Soc. J.* xxxii. 944).

Purification from Arsenic.—H. A. Smith (*Amer. Chemist*, 1873, 413) observes that the process of heating the sulphuric acid with common salt, or passing hydrochloric acid gas through it, never effects a complete removal of the arsenic. Better results are obtained with hydrogen sulphide, the best mode of proceeding being to mix the sulphuric acid with a sufficient quantity of iron sulphide, or of sodium sulphide in case the introduction of iron into the acid should be objectionable. The metallic sulphide is added to the acid in a leaden pan containing a layer of coke, which serves as a filter, and covered with a perforated lid, through which the excess of hydrogen sulphide can escape.

W. Thorn (*Dingl. pol. J.* ccxvii. 495) observes that in many sulphuric acid works, the removal of the arsenic is effected by sodium thiosulphate. Chamber-acid of 50° B. is heated to 70° – 80° , and a quantity of thiosulphate equivalent to the arsenic present is added either in concentrated solution or in the form of powder. After the mixture has been sufficiently stirred, the arsenic separates on the surface in flocks of arsenious sulphide. The purified acid is withdrawn from under the flocks; the leaden vessel is again charged with chamber-acid, and after several repetitions of the operation, the arsenious sulphide is collected. The crude sulphuric acid contained 0.098 per cent. arsenic, the purified acid 0.004 per cent., together with 0.3 to 0.4 per cent. sodium sulphate.

With regard to this process, R. Wagner remarks (*ibid.* ccxviii. 321) that if the contamination of the acid with sodium sulphate is not objectionable, sulphide of sodium

is preferable to the thiosulphate; if, on the other hand, such contamination must be avoided, he recommends barium thiosulphate as the purifying agent, the reaction taking place as follows:



19·8 pts. arsenious oxide require 85·5 pts. $\text{BaS}^2\text{O}^3 + \text{H}^2\text{O}$.

With regard to the distribution of the arsenic occurring in pyrites in sulphuric acid and the products of the soda-manufacture prepared therewith, C. Hjelt shows (*Dingl. cexvi. 174*) that the amount of arsenic in pyrites is very variable, Spanish pyrites containing 0·12 per cent., Westphalian 0·3, and Norwegian only traces of arsenic. He found also that in a sulphuric acid made from Spanish pyrites the average amount of arsenic, reckoned on pure hydrogen sulphate, H^2SO^4 , was:

	Arsenio p. c.	Present as arsenic acid p. c.
In chamber-acid.	0·202	0·040
In acid from the Glover tower	0·331	0·041
In acid from the Gay-Lussac tower . .	0·344	0·132

He also directs attention to the fact that the loss of nitric acid in sulphuric acid works is due, at least in part, to the arsenic in the acid—that is to say in the pyrites—inasmuch as, in the Gay-Lussac tower, part of the nitrous acid is reduced by the arsenic in the sulphuric acid to nitrogen dioxide. In accordance with this view, it is found that the larger the proportion of arsenic in the pyrites used, the greater is the loss of nitric acid. In well-conducted alkali-works, the arsenic of the sulphuric acid never goes into the sodium sulphate, but is all found in the hydrochloric acid produced at the same time, none of it, however, passing into the bleaching-powder. In the burnt residues of Spanish pyrites, Hjelt found only 0·19 per cent. arsenic.

A description of the apparatus used at the Freiberg works for purifying sulphuric acid from arsenic is given by F. Bode (*Dingl. cexiii. 25*).

Concentration.—Apparatus for the Concentration of Sulphuric acid is described by F. Bode (*Dingl. cxi. 26; cexiii. 204; cexvi. 326; Jahresh. f. Chem. 1874, 1107; 1875, 1053*).

Estimation.—The following method for the quantitative analysis of a mixture of sulphates of alkalis and alkaline earths (magnesia and lime) is described by Jean a. Pellet (*Bull. Soc. Chim. [2], xxvii. 203*). To determine the sulphuric acid in combination with the alkalis, the mixture of salts, dissolved, if necessary, with addition of hydrochloric acid, and carefully neutralised, is mixed with excess of barium hydrate, then with water containing carbonic acid, heated till the carbonic acid is expelled, and the weighed filtrate is titrated with sulphuric acid. The calcium sulphate is precipitated by alcohol from a measured volume of the solution, decomposed by boiling with a titrated solution of sodium carbonate, and the excess of the latter is determined by back titration. Magnesium sulphate is also decomposed by sodium carbonate and estimated in like manner by titration. To determine the total amount of sulphuric acid, free and combined, the sulphates are boiled with solution of sodium carbonate, and the liquid is filtered, neutralised with standard sulphuric acid, and treated with baryta as above. This method may be applied to the estimation of sulphates in pyrites.

To determine the amount of free sulphuric acid in vinegar, J. C. Thresh (*Pharm. J. Trans. [3], vi. 1*) adds a known quantity of barium chloride, evaporates and incinerates the whole, and calculates the free sulphuric acid from the loss of hydrochloric acid thence ensuing.

According to A. Hilger (*Arch. Pharm. [3], vi. 510*), the detection of free sulphuric acid in vinegar is best effected by means of sugar, which, if sulphuric acid is present, is blackened when the liquid is evaporated to dryness.

On the Methods of Estimating Sulphuric acid in Water, see Tiemann (*Ber. vi. 918; Jahresh. f. Chem. 1873, 903*).

Hydrates.—According to Pierre a. Puchot (*Ann. Chim. Phys. [5], ii. 164*), the 'dihydrate,' $\text{SO}^3\cdot 2\text{H}^2\text{O}$ or $\text{SO}^4\cdot \text{H}^2\cdot \text{H}^2\text{O}$, melts and solidifies at $7\cdot 5^\circ$, but afterwards exhibits superfusion. 3 pts. of the crystallised hydrate and 8 pts. of snow produced a fall of temperature to $-26\cdot 25^\circ$, whereas with an equal quantity of liquid acid, the temperature fell only to $-19\cdot 5^\circ$. On cooling a sulphuric acid intermediate between $\text{SO}^3\cdot \text{H}^2\text{O}$ and $\text{SO}^3\cdot 2\text{H}^2\text{O}$ (63°B.), part of it crystallised, and the liquid decanted therefrom exhibited a higher concentration. A more dilute acid did not crystallise at -8° to -10° , even when small crystals of the dihydrate were thrown into it.

METALLIC SULPHATES. The action of dry hydrogen chloride on these salts has been examined by C. Hensgen (*Ber.* ix. 1671, 1674; x. 259). *Potassium sulphate* is not attacked by the dry gas either at ordinary or at lower temperatures; at 100° the crystals become corroded at certain points; at 360°, the water into which the gas passes is found to contain a weighable quantity of sulphuric acid; and at a dull red heat, the salt is converted almost quantitatively into potassium chloride and free sulphuric acid. *Anhydrous sodium sulphate* is likewise completely decomposed by hydrogen chloride at high temperatures; crystallised Glauber's salt, $\text{Na}^2\text{SO}^4 + 10\text{H}^2\text{O}$, on the other hand, is completely converted at ordinary temperatures, and even at -17° , though less quickly, into sodium chloride. The Glauber's salt first melts in its water of crystallisation, with considerable reduction of temperature (-17°), but the temperature quickly rises, and remains during the decomposition at 53° – 55° , and the resulting sodium chloride separates in the form of a fine-grained powder. *Anhydrous lithium sulphate*, Li^2SO^4 , behaves like the anhydrous sulphates of the other alkali-metals; the hydrate, $\text{Li}^2\text{SO}^4 + \text{H}^2\text{O}$, decomposes completely, even at ordinary temperatures, melting in its water of crystallisation, and taking up hydrogen chloride with considerable evolution of heat. The sulphates of calcium, strontium, and barium are likewise completely decomposed by HCl at a dull-red heat, as formerly shown by Boussingault. *Magnesium sulphate*, MgSO^4 , is not attacked by dry hydrogen chloride at any temperature below commencing redness, but with the hydrated salt, $\text{MgSO}^4 + 7\text{H}^2\text{O}$, the action begins at ordinary temperatures. The crystals melt to a clear liquid, which after a while deposits a crystalline powder, soon in such quantity that the whole solidifies to a stiff crystalline pulp. The composition of these crystals (disregarding a small amount of chlorine) is most nearly expressed by the formula $\text{MgSO}^4 + 6\text{H}^2\text{O}$. The absorption of hydrogen chloride (12.52 p. c.) by the salt $\text{MgSO}^4 + 7\text{H}^2\text{O}$ was probably due to the water of crystallisation, and not to decomposition of the salt into magnesium chloride and sulphuric acid. *Dehydrated cupric sulphate*, CuSO^4 , is strongly attacked by dry hydrogen chloride, of which it takes up 2 mol., at the same time becoming hot, acquiring a dark brown colour, losing its pulverulent consistence, and caking together to a damp mass which gives up all its hydrogen chloride when exposed to the air or when heated. Hydrated cupric sulphate, $\text{CuSO}^4 \cdot 5\text{H}^2\text{O}$, is completely decomposed by dry hydrogen chloride, according to the equation $\text{CuSO}^4 + 2\text{HCl} = \text{CuCl}^2 + \text{H}^2\text{SO}^4$, the chloride separating in green needles having the composition $\text{CuCl}^2 \cdot 2\text{H}^2\text{O}$.

Ethyl sulphates are not decomposed by dry hydrogen chloride at ordinary temperatures. The *potassium salt* remains quite unaltered; the *barium salt* absorbs the gas, with rise of temperature, the gas abstracting the water of crystallisation and dissolving therein. Between 65° and 85° , however, both these salts are decomposed, with evolution of ethyl chloride and formation of potassium disulphate in the one case, and of barium sulphate and sulphuric acid in the other (H. Köhler, *Ber.* xi. 1929).

Conversion of Sulphates into Carbonates, &c.—Alkaline sulphates may be converted into carbonates by dissolving them in carbonic acid water, and mixing them with $1\frac{1}{2}$ time their weight of barium carbonate rubbed to a thick paste with a little water, agitating the mixture strongly for some time, and finally heating it to the boiling point: the filtered liquid will then be found to contain nothing but carbonates. To convert an alkaline sulphate into the corresponding *tartrate*, *oxalate*, &c., it is heated in a porcelain basin with barium carbonate and water, and the requisite quantity of tartaric or oxalic acid is gradually added (L. Smith, *Amer. Chem.* 1873, iii. 241).

Aluminium sulphate.—The presence of free sulphuric acid in this salt may be quickly detected by stirring up the pulverised salt in alcohol. The salt is insoluble in this liquid, but free sulphuric acid dissolves in it, and may be recognised by its acid reaction, or estimated by titration. Pure aluminium sulphate gives with decoction of logwood a blue-violet coloration, but the presence of free sulphuric acid gives rise to a brown colour.

Ammonium sulphate.—The normal salt, $(\text{NH}^4)^2\text{SO}^4$, is formed in the combustion of coal-gas, and collects as a sublimate of short anhydrous prisms on the shades placed over the burners (Priwoznik, *Dingl.* cccxiii. 223).

Several acid salts are formed by the action of heat on the normal salt. $(\text{NH}^4)\text{HSO}^4$ is produced when the normal salt is heated till the thick pasty mass ceases to give off ammonia. $(\text{NH}^4)^2\text{H}^4(\text{SO}^4)^3$ is formed when the preceding salt is more strongly heated, the heat being continued till the intumescence has subsided. By keeping the temperature somewhat lower, a third salt is obtained, having the composition $(\text{NH}^4)^3\text{H}^4(\text{SO}^4)^3$ (P. Schweitzer, *Amer. Chem.* vii. 42). These acid ammonium sulphates have also been examined by S. W. Johnson and R. H. Chittenden (*Sill. Am. J.* [3], xv. 131), whose analyses agree with those of Schweitzer so far as regards the amounts of sulphuric

acid, but differ considerably therefrom in the proportions of ammonia and water. They also show that Schweitzer's bisulphate still retained a portion of the normal sulphate, and hence conclude that it was a mixture of 1 mol. ammonium pyrosulphate, $(\text{NH}_4)_2\text{S}_2\text{O}_7$, 1 mol. normal sulphate, $(\text{NH}_4)_2\text{SO}_4$, and 3 mols. bisulphate, $(\text{NH}_4)\text{HSO}_4$. In like manner, they show that the so-called trisulphate, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_3$, may be regarded as a mixture of 1 mol. pyrosulphate and 2 mol. bisulphate.

Barium Sulphate, BaSO_4 , may be obtained in crystals, partly grouped, by heating a dilute solution of the chloride with a slight excess of sulphuric acid at 245° (Scheerer a. Drechsel, *J. pr. Chem.* [2], vii. 63. When a solution of barium sulphate (14 pts.) in 100 pts. strong sulphuric acid (sp. gr. 1.843) was heated at 100° , a considerable number of needle-shaped crystals separated out. At 160° – 180° these crystals disappeared, and prismatic crystals began to separate, their quantity becoming greater the nearer the temperature of the liquid approached to the boiling point of the acid. At the latter temperature, 10 pts. of the acid still held in solution from 8.5–9 pts. of barium sulphate. On the other hand, the needles which separated at 100° were insoluble in the cold acid (T. Graside, *Chem. News*, xxxi. 245).

According to G. Brügelmann (*Zeitschr. anal. Chem.* x. 22), the process recommended by Fresenius (vii. 1128) for purifying the barium sulphate obtained in quantitative analyses does not always answer its purpose. Good results are, however, obtained when the ignited sulphate is triturated with 3 or 4 drops of strong hydrochloric acid and a few drops of water, then boiled with water and filtered, the process being repeated five times in the same manner.

Calcium Sulphate.—According to Pollacci (*Gazz. chim. ital.* 1874, 177, 245), gypsum, $\text{CaSO}_4 + 2\text{H}_2\text{O}$, is formed in a mixture of calcium carbonate and sulphur moistened with water, and the action is assisted by the organic matters in vegetable soil. In the hottest days of summer, 20–25 grams of material is sufficient to yield a small quantity of gypsum in three hours. According to Perugnatelli a. Pelloggio (*Ber. vii.* 1462), sodium thiosulphate is formed at the same time. The carbonates of barium, strontium, and magnesium are converted into sulphates under like conditions, the action being slowest in the case of the magnesium salt. Pollacci attributes the transformation to a direct oxidation of sulphur: $\text{S}^2 + 3\text{O}^2 + 2\text{H}_2\text{O} = 2\text{SO}_4\text{H}^2$. In those cases in which calcium carbonate is said to be converted into gypsum under the influence of hydrogen sulphide, this compound does not appear to be directly oxidised, but to be decomposed by the oxygen of the air, with separation of sulphur, which then undergoes oxidation.

According to Cossa (*Gazz.* 1873, 135), 1000 pts. water dissolve 2.119 pts. gypsum at 16.5° , and 2.352 pts. at 22° . A saturated solution of gypsum acts on rocks containing alkaline silicates (gneiss, trachite, granite, felspar, basalt) much more readily than pure water, taking up in a given time a much larger quantity of soluble constituents. According to Asselin (*Compt. rend.* lxxvi. 884), 100 pts. of glycerol dissolve 0.957 pt. of gypsum at ordinary temperatures, and a continually larger quantity as the temperature rises.

Double Salts of Calcium Sulphate.—The following are described by R. Fassbender (*Ber.* ix. 1358; xi. 1968). The salt $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, first observed by Phillips, H. Rose, and others, and obtained by Struve (*Bull. Soc. Chim.* [2], xii. 348) on treating gypsum with a solution of potassium nitrate, chloride, or iodide, is also readily formed by dissolving potassium sulphate in a saturated solution of gypsum, the separation of the salt in slender silky needles beginning almost immediately, and going on for several months. The same double salt is obtained by treating solid gypsum with solution of potassium sulphate, and by dissolving potassium sulphate in a solution of potassium nitrate or chloride saturated with gypsum, a portion of the potassium nitrate or chloride, however, adhering to the product with great obstinacy (Fassbender); also, according to Ditte (*Compt. rend.* lxxxiv. 86), on adding sulphuric acid to a mixture of the two component sulphates, and boiling the liquid. The calcium sulphate then collects at the bottom in the form of a white powder, but in the course of twenty-four hours the whole solidifies to well-defined transparent flattened prismatic crystals of the double salt. These crystals lose their lustre and become anhydrous when heated, and are completely decomposed by water. When, on the other hand, calcium sulphate, either anhydrous or hydrated, is added to a saturated solution of potassium sulphate, the double salt, $\text{Ca}^2\text{K}^2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$, separates almost instantly in spangles or small needles having a nacreous lustre. This salt is decomposed by cold water, which gradually abstracts all the potassium sulphate.

A Calcium-ammonium Sulphate, $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, which, according to Popp (*Liebig's Annalen*, 8 Suppl. 1), is obtained on evaporating the water of the Tuscan lagoons, may also be produced artificially by dissolving 285 grams of ammonium sulphate in 800 c.c. water, saturating the solution with gypsum, evaporating to 600–

500 c.c., and filtering at 40–50. This degree of concentration appears to be essential, inasmuch as the salt is resolved into its constituents by water (Fassbender). Ditte prepares this salt, like the corresponding potassium salt, by adding sulphuric acid to a mixture of the sulphates of calcium and ammonium, and boiling the liquid. It crystallises in needles which have a very strong lustre, and are instantly decomposed by water. The sulphates of sodium and lithium do not appear to unite under similar circumstances with calcium sulphate.

A *Calcium-potassium-ammonium Sulphate*, $\text{CaSO}_4 \cdot (\text{KNH}_4)\text{SO}_4 \cdot \text{H}_2\text{O}$, is obtained by adding potassium sulphate to a solution of ammonium sulphate saturated with gypsum; by digesting calcium-potassium sulphate with solution of ammonium sulphate; or by digesting gypsum with solutions of potassium and ammonium sulphates. Analogous sodium salts do not appear to exist; moreover, the above-mentioned double salts are decomposed by saturated solutions of sodium sulphate or other sodium salts, with separation of gypsum.

If, in a saline solution saturated with calcium sulphate, the solubility of that salt be diminished by the introduction of another salt, the calcium sulphate will be precipitated as gypsum or as anhydrite, according as the solution is at ordinary temperature or at the boiling heat. This reaction is best shown by adding magnesium sulphate to a solution saturated with common salt and gypsum (Fassbender).

Calcium-rubidium Sulphate, $\text{Ca}^2\text{Rb}^2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$, prepared like the corresponding potassium salt, crystallises in stellate groups of translucent needles, which are decomposed by water (Ditte).

A number of remarkable double salts of calcium sulphate have been found by J. B. Hannay amongst the crystalline precipitates deposited in tubes through which have been successively passed solutions of K^2SO_4 , Na^2SO_4 , CaSO_4 , MgSO_4 and K^2CrO_4 , the last in excess. The greater number of the layers thus formed consisted of $\text{CaK}^2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, but there were also found two double salts of potassium chromate, consisting respectively of $\text{Ca} \cdot \text{K}^2(\text{SO}_4)(\text{CrO}_4) \cdot \text{H}_2\text{O}$ and $\text{CaK}^2(\text{SO}_4)(\text{CrO}_4)_2$. These two salts, scarcely distinguishable from one another in external appearance, form flat prisms of undeterminable form, but having a brilliant aspect like that of lead iodide; they are resolved by water into potassium chromate and pure calcium sulphate. Associated with the latter of these two salts was found a mass having a dark colour and no determinate crystalline structure, but appearing under the microscope to be made up of small felted needles, and having the composition $\text{CaSO}_4 \cdot \text{Na}^2\text{SO}_4 \cdot \text{K}^2\text{CrO}_4$. In another tube through which large quantities of the salt $\text{CaNa}^2(\text{SO}_4)_2$ had passed, a deposit was formed resembling the salt above described, but differing from it by containing water of crystallisation: its composition was $\text{CaSO}_4 \cdot \text{Na}^2\text{SO}_4 \cdot \text{K}^2\text{CrO}_4 + \text{H}_2\text{O}$. Hannay also describes a compound of calcium sulphate with hydrogen chloride. When a solution of calcium sulphate in hydrochloric acid is evaporated in a flask having its neck drawn out, and the residual gas is displaced by air without cooling the flask, a residue is left the composition of which agrees best with the formula $2\text{CaSO}_4 \cdot \text{HCl} + 3\text{H}_2\text{O}$, which is that of the normal salt $2\text{CaSO}_4 + 4\text{H}_2\text{O}$, having $1\text{H}_2\text{O}$ replaced by 1HCl (*Chem. Soc. J.* xxxii. 399).

Cerium Sulphates. See CERIUM (p. 421).

Chromic Sulphate, $\text{Cr}^2(\text{SO}_4)_3$.—Etard (*Compt. rend.* lxxiv. 1089) prepares this salt by passing ether-vapour into a solution of 100 pts. chromic acid, 150 sulphuric acid, and 225 water, whereby, after some time, a dense crystalline mass is formed, which, after washing with ether and drying, consists of small lamellæ, having a beautiful violet colour, permanent in the air, and having, when air-dried, the composition $\text{Cr}^2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$. Schrötter, on the other hand, obtained the salt with $15\text{H}_2\text{O}$ (v. 588). When dried at 100° it gives off $12\text{H}_2\text{O}$, and is converted into a crystallised deliquescent salt belonging to the green modification. Hence it appears that the difference between the green and violet modifications of chromic salts is due to the different amounts of water which they contain, and that the passage from the violet to the green modification on heating must be attributed to an abstraction of water, which may take place even within the solution, and thereby depends upon a true dissociation. In confirmation of this view, Etard has treated the violet sulphate with dehydrating agents, such as strong nitric acid, sulphuric acid, and phosphorus trichloride, and finds that a conversion of the violet into the green modification takes place in every instance. He remarks that the complete conversion of a chromic salt into the green modification can be ascertained only by observation with artificial light, inasmuch as many chromic solutions appear green in sunlight, although they still contain considerable quantities of violet salt (Etard).

According to Lecoq de Boisbaudran (*Compt. rend.* lxxix. 1491), blue solutions of chrome-alum prepared in the cold gradually assume a green colour, and the green solutions prepared at higher temperatures gradually turn blue, these changes taking

place either in open or in closed vessels, in dilute or in strong solutions, and independently of contact with crystals. The first change is attended with dehydration of the blue salt and gradual increase of the volume of the solution; the second with hydration and gradual diminution of volume. The rate of conversion of the green into the blue salt diminishes rapidly with the time elapsed after cooling, an increase of volume being still perceptible after a month, and the state of equilibrium does not appear to be attained till after the lapse of eight years.

The double salt, $\text{Cr}^2(\text{KSO}^4)^2$, is obtained in yellowish-green felted needles by adding small quantities of chromic chloride to melting potassium bisulphate; and the corresponding sodium salt is obtained in like manner, though less easily, as a crystalline sandy powder (Etard).

On Double Sulphates of Chromium, see also p. 458.

Copper Sulphates.—A hydrate, having the composition $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, is obtained as an amorphous powder when the ordinary pentahydrate is heated at 25° – 30° in dry air. It is especially characterised by remaining quite unaltered in a vacuum, whereas the pentahydrate left in a vacuum at the same temperature gives off 4 mol. water (Magnier de la Source, *Compt. rend.* lxxxiii. 899). Another hydrate, formed in the preparation of the copper salt of benzenesulphonic acid, crystallises in large, thin, blue laminae, containing a small quantity of the benzenesulphonate (Ozier, *Ber.* ix. 83).

On the Dissociation of Cupric Sulphate, see p. 1013; on its reaction with HCl , see p. 1872.

Didymium Sulphate, $\text{Di}^2(\text{SO}^4)^3 \cdot 9\text{H}_2\text{O}$. See DIDYMIUM (pp. 425, 644).

Iron Sulphates.—*Ferrous and Ferric Sulphates* are formed, together with free sulphuric acid and hydrogen sulphide, when iron pyrites is heated with water at 120° in a sealed tube (C. A. Burghardt, *Chem. News*, xxxvii. 49).

Double Sulphates of Iron and Allied Metals (Etard, *Compt. rend.* lxxvi. 1399; lxxxvii. 602). 1. *Ferrico-aluminic salts.*—When 2 mols. ferrous sulphate and 1 mol. aluminium chloride are dissolved in the smallest possible quantity of hot water, the ferrous salt oxidised with nitric acid, a large excess of strong sulphuric acid added, and the liquid heated to about 220° , a crystalline precipitate separates composed of microscopic hexagonal plates, which when freed by decantation from excess of sulphuric acid, washed with glacial acetic acid, and dried at 120° , exhibit the composition $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{Al}^2(\text{SO}^4)^3 \cdot \text{H}^2\text{SO}^4$. This salt, when heated to redness, gives off sulphuric acid, and leaves a white crystalline salt, insoluble in water, and having the composition $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{Al}^2(\text{SO}^4)^3$.

2. *Ferrico-chromic Salts.*—The salt $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{Cr}^2(\text{SO}^4)^3 \cdot \text{H}^2\text{SO}^4$ is obtained in like manner, with molecular proportions of ferrous sulphate and chromic acid, as a yellowish crystalline precipitate insoluble in water. When strongly heated, it likewise gives off sulphuric acid, leaving the insoluble and very stable salt, $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{Cr}^2(\text{SO}^4)^3$.

Alumino-chromic Sulphate, $\text{Al}^2\text{Cr}^2(\text{SO}^4)^6 \cdot \text{H}^2\text{SO}^4$, is obtained in a similar manner, as a light-green crystalline precipitate, which when heated gives off H^2SO^4 , leaving $\text{Al}^2\text{Cr}^2(\text{SO}^4)^6$.

Manganico-aluminic Sulphate, $\text{Mn}^2(\text{SO}^4)^2 \cdot 2\text{Al}^2(\text{SO}^4)^3$, is formed when a mixture of manganous sulphate and aluminium sulphate is treated as above, and a mixture of sulphuric and nitric acids in equal volumes is added by small portions to the liquid previously heated to 250° . At this temperature the manganous sulphate is raised to a higher state of oxidation, nitrous fumes are evolved, the originally colourless solution turns violet, and the double salt separates as a fine blue precipitate insoluble in water.

Manganese-iron Sulphates.—The salt $\text{Fe}^2(\text{SO}^4)^2 \cdot 2\text{MnSO}_4 \cdot 3\text{H}^2\text{SO}^4$ is prepared in a similar manner, using ferrous sulphate instead of aluminium sulphate, and separates at about 160° , as a light-yellow well-crystallised salt, which is soluble in water, and when heated gives off $2\text{H}^2\text{SO}^4$, and is converted into $\text{Fe}^2(\text{SO}^4)^2 \cdot 2\text{MnSO}_4 \cdot \text{H}^2\text{SO}^4$, which has a darker yellow colour and is insoluble in cold water. In these two salts the manganese is not raised to a higher stage of oxidation, but if the oxidising mixture of nitric and sulphuric acid be poured into the strongly heated solution without previously separating the yellow precipitate, the salt $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{Mn}^2(\text{SO}^4)^2$, gradually separates in the form of a deep green crystalline precipitate insoluble in water.

Manganese-chromium Sulphates.—If in the process last described the iron salt be replaced by chromic acid, the salt $\text{Mn}^2(\text{SO}^4)^2 \cdot \text{Cr}^2(\text{SO}^4)^3$ is obtained in the form of a green precipitate, and if the solution, after being heated with sulphuric acid, be left to cool before a precipitate is deposited from it, brown tabular crystals are obtained, consisting of the salt $\text{Mn}^2(\text{SO}^4)^2 \cdot \text{Cr}^2(\text{SO}^4)^3 \cdot 2\text{H}^2\text{SO}^4$, which dissolves with decomposition in water, and when heated in the air is reduced to a green powder, $\text{Cr}^2(\text{SO}^4)^3 \cdot 3\text{MnSO}_4$, and a white basic salt.

A rose-coloured *acid ferroso-ferric sulphate*, $\text{Fe}^2(\text{SO}^4)^2 \cdot \text{FeSO}_4 \cdot 2\text{H}^2\text{SO}^4$, is sometimes

found at the bottom of the platinum vessels used for the concentration of sulphuric acid, and may be easily prepared by dissolving ferrous and ferric sulphates (1 mol. of each) in the smallest possible quantity of water, adding a large excess of strong sulphuric acid, and heating the liquid to 200°, avoiding as much as possible the contact of air or other oxidising agents. The liquid on cooling deposits the double sulphate in small six-sided plates having a peach-blossom colour. In a similar manner the following salts may be obtained:

$\text{Cr}^2(\text{SO}^4)^3, \text{NiSO}^4, 2\text{SO}^4\text{H}^2 + 3\text{H}^2\text{O}$:	greenish-yellow.
$\text{Cr}^2(\text{SO}^4)^3, 2\text{FeSO}^4, \text{SO}^4\text{H}^2 + 2\text{H}^2\text{O}$:	brownish-green.
$\text{Cr}^2(\text{SO}^4)^3, 2\text{CuSO}^4, \text{SO}^4\text{H}^2$:	greenish, asbestos-like needles, having a silky lustre.
$\text{Fe}^2(\text{SO}^4)^3, \text{NiSO}^4, 2\text{SO}^4\text{H}^2$:	yellow, crystalline.
$\text{Fe}^2(\text{SO}^4)^3, 2\text{MnSO}^4, 3\text{SO}^4\text{H}^2$:	light-yellow, well-crystallised laminæ.
$\text{Al}^2(\text{SO}^4)^3, 2\text{FeSO}^4, \text{SO}^4\text{H}^2$:	white six-sided laminæ.
$\text{Al}^2(\text{SO}^4)^3, 2\text{NiSO}^4, \text{SO}^4\text{H}^2$:	yellowish, crystalline mass.

All these salts are insoluble in water, and are gradually decomposed thereby. Corresponding manganese salts may also be obtained, but they are difficult to purify.

Double sulphates of diatomic metals (magnesium group) of the general formula $(\text{M}^2\text{SO}^4, \text{R}^2\text{SO}^4)^2, \text{H}^2\text{SO}^4$ may be prepared by similar processes: the following have been obtained:

$(\text{NiSO}^4, \text{ZnSO}^4)^2, \text{SO}^4\text{H}^2$:	yellowish.
$(\text{FeSO}^4, \text{ZnSO}^4)^2, \text{SO}^4\text{H}^2$:	rose-coloured.
$(\text{CuSO}^4, \text{ZnSO}^4)^2, \text{SO}^4\text{H}^2$:	"
$(\text{CuSO}^4, \text{CoSO}^4)^2, \text{SO}^4\text{H}^2$:	"
$(\text{FeSO}^4, \text{CoSO}^4)^2, \text{SO}^4\text{H}^2$:	"
$(\text{CuSO}^4, \text{NiSO}^4)^2, \text{SO}^4\text{H}^2$:	"

The sulphates of iron and copper yield in like manner a red crystalline double salt, $\text{CuSO}^4, \text{FeSO}^4 + 2\text{H}^2\text{O}$, which does not give up its water of crystallisation till somewhat strongly heated, and is not oxidised even by fuming nitric acid. In the same manner have been obtained the salts $\text{CuSO}^4, \text{MnSO}^4 + \text{H}^2\text{O}$ and $\text{CuSO}^4, \text{NiSO}^4 + 3\text{H}^2\text{O}$. By similar treatment of the simple salts instead of the mixtures, the mono- and di-hydrated salts are easily obtained in crystalline form, e.g. $\text{CoSO}^4 + \text{H}^2\text{O}$, $\text{NiSO}^4 + 2\text{H}^2\text{O}$, $\text{ZnSO}^4 + \text{H}^2\text{O}$, $\text{CuSO}^4 + \text{H}^2\text{O}$. By dissolving the simple salts in strong sulphuric acid and boiling the solutions, the anhydrous salts are obtained in crystalline form, e.g. CoSO^4 , in hexagonal prisms with pyramidal summits at each end, and having the aspect and reddish colour of some kinds of quartz; also NiSO^4 in lemon-yellow crystals of similar aspect, and CuSO^4 in fine white prisms (Etard).

Lead Sulphate, PbSO^4 .—On the crystalline form of Hungarian lead sulphate, see Krenner (*Zeitschr. Kryst.* i. 321; *Jahresb. f. Chem.* 1877, 1295).

Solubility.—J. Kolb (*Dingl. pol. J.* ccix. 268) has determined the solubility of this salt in sulphuric acid of different strengths and at ordinary temperatures, with the following results:

100 pts. acid of sp. gr. 1.841	dissolve	0.039 pt. PbSO^4
" " " 1.793	"	0.011 "
" " " 1.540	"	0.003 "

The solubility is increased by the presence of nitric acid, but not by that of sulphurous acid.

In **Acetates**. According to H. C. Dibbits (*Zeitschr. anal. Chem.* 1874, 137), 100 pts. of water containing a drop of acetic acid, and

2.05 pts. sodium acetate	dissolve	0.054 pt. PbSO^4
8.2 " " "	"	0.900 "
41.0 " " "	"	11.200 "

The quantity of lead sulphate dissolved appears to be but little influenced by temperature. The solution is immediately precipitated by sulphuric acid and by lead acetate. On mixing the solution with 7 vols. alcohol of 92 per cent. a precipitate is formed consisting of anhydrous sodium sulphate and lead sulphate, in one instance 89.4 per cent. Na^2SO^4 and 10.6 PbSO^4 , in another 96.0 Na^2SO^4 and 4.0 PbSO^4 . Lead sulphate also dissolves in the acetates of manganese, zinc, nickel, and copper, but not in acetate of mercury or silver. Barium acetate and lead sulphate decompose one another partially at ordinary temperatures, producing lead acetate and barium sulphate; the converse reaction does not take place.

Reactions.—Lead sulphate, treated with excess of *potassium iodide*, is readily con-

verted into lead iodide, or the double iodide of lead and potassium. When lead sulphate (1 mol.) and *sodium chloride* (1 mol.) in solution are brought together in presence of lead oxide, about half of the material is converted into lead chloride and sodium sulphate. The quantity of lead oxide may be varied to a considerable extent without perceptible effect on the intensity of the reaction. After several repetitions of the treatment with sodium chloride, at each of which a similar action takes place, there finally remains a mixture containing, together with a small quantity of unaltered lead sulphate, a double salt of lead chloride and carbonate easily decomposed by water (F. Matthey, *Arch. Pharm.* [3], xiii. 233).

Lithium Sulphate.—An acid lithium sulphate, $\text{LiHSO}_4 \cdot \text{H}^2\text{SO}_4$, is obtained in deliquescent crystals melting at 120° , by dissolving the normal salt in pure hydrogen sulphate, H^2SO_4 (Nordhausen acid from which the anhydride had been distilled off) (Lescœur, *Bull. Soc. Chim.* [2], xxiv. 516).

Magnesium Sulphate.—On the dehydration of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, by heating in a current of air, see Hannay (p. 1014). On its decomposition by dry hydrogen chloride, Henagen (p. 1872).

To detect the presence of alkali-sulphates in commercial magnesium sulphate, E. Biltz (*Zeitschr. anal. Chem.* x. 258) triturates 2 grams of the salt with 2 g. dry calcium hydrate prepared from burnt marble; then adds water in sufficient quantity to convert the mixture into a granular powder; drenches the mass with 5 g. of a mixture of equal parts alcohol of 90 degrees and water; and, after agitation, leaves it at rest for an hour, and lastly adds 10 g. absolute alcohol. If alkali-salts are present (from $\frac{1}{2}$ per cent. upwards), turmeric paper in contact with the mixture immediately turns brown.

Manganese Sulphates. See MANGANESE (p. 1266). On Double Manganese Sulphates, p. 1876.

Mercuric Sulphate.—The compound $\text{HgSO}_4 \cdot 2\text{HCl}$, or more probably $\text{HgCl}_2 \cdot \text{H}^2\text{SO}_4$, is formed by the action of gaseous hydrogen chloride or of strong hydrochloric acid on mercuric sulphate. It is fusible, and sublimes in white needles. The corresponding bromine-compound, formed in like manner, sublimes in white shining laminae. Both these compounds dissolve in water without decomposition (A. Ditte, *Compt. rend.* lxxxvii. 794).

Nickel Sulphates, Double (p. 1876).

Philippium Sulphate. See YTTRIUM METALS.

Potassium Sulphates.—In preparing the normal sulphate K_2SO_4 from kieserite, $2\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and potassium chloride, G. Berscho proposes first to prepare the double sulphate of magnesium and potassium, and then convert this salt by means of potassium chloride into potassium sulphate and magnesium-potassium chloride. The reaction is somewhat retarded by the presence of the magnesium chloride, but this inconvenience may be avoided by treating a mixture of 5 to 8 mols. potassium chloride and 4 mols. magnesium sulphate with successive small quantities of cold or moderately warm water, not sufficient in all to dissolve the salt completely. The residue then consists of pure potassium sulphate. The greater part of the magnesium chloride remains in the first mother-liquors, and the later mother-liquors, which contain less magnesium, may be used to decompose fresh quantities of kieserite, whereby the yield of potassium sulphate is increased, and chloride of potassium is saved. For evaporation there is always obtained a determinate quantity of mother-liquor of constant composition, which deposits carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, available for the preparation of potassium chloride.

F. Bräjes has patented a process for preparing potassium sulphate from kainite and from kieserite, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, which consists in dissolving 1.5 to 2 mols. potassium chloride and 1 mol. kieserite or kainite (in the latter case with addition of 1 mol. KCl) in 460–600 pts. water, and precipitating with alcohol. The whole of the magnesium then remains dissolved as chloride, and any potassium chloride that may remain in excess is partially precipitated with the sulphate. On evaporating the mother-liquor to 30°B , an additional quantity of pure potassium chloride separates out, followed, on further concentration to 36°B , by carnallite. An excess of potassium chloride is necessary in this process, so that the precipitated sulphate may be rendered loosely coherent by the admixture with the chloride, and the washing thereby facilitated (*Jahresb. f. Chem.* 1878, 1127).

J. Ogier (*Compt. rend.* lxxxii. 1055), in preparing the potassium salt of benzenesulphonic acid, has obtained a new form of normal potassium sulphate, differing from the ordinary form by containing a smaller amount of crystallisation-water. It crystallises in large transparent plates, having the composition $\text{K}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and gives off its water in a vacuum or when heated to 150° . 100 pts. of water at 15° dissolve

9.82 pts. of this salt. The same salt is obtained by crystallisation of a mixture of potassium sulphate and benzenesulphonate containing an excess of the latter.

An *acid potassium sulphate*, $K^2O, 4SO^2 + 6H^2O$, or perhaps $K^2H^2(SO^4)^2 + 3H^2O$, is obtained by dissolving the normal salt in hot strong sulphuric acid, and separates on cooling in large nacreous deliquescent crystals which melt at 61° , and give off water at 235° (H. Lesceur, *Compt. rend.* lxxviii. 1044).

Sodium Sulphate, Na^2SO^4 .—On the solubility of this salt in glass, see Ebell (*Dingl. pol. J.* cccxv. 168; *Jahresb. f. Chem.* 1877, 1165).

On the analysis of crude sodium sulphate (*Ball-soda*), see Tate, Tinniswood, and Simmonds (*Chem. News*, xxix. 144, 164, 185, 205, 216, 239).

Sodio-ferrous Sulphate, $Na^2Fe(SO^4)^2 \cdot 4H^2O$, may be prepared by dissolving crystallised ferrous sulphate, in its own weight of hot water, with addition of 2 per cent. dilute sulphuric acid, and adding an equivalent quantity of crystallised sodium sulphate (100 pts. to 88.8 ferrous sulphate), then heating the solution to the boiling point, and evaporating it with gentle ebullition and constant stirring. The double salt which separates out is drained, washed with a little cold water, and dried, first in the air of a warm room, and finally at 100° , at which temperature it does not give off its water of crystallisation (Biltz, *Zeitschr. anal. Chem.* 1874, 174).

Strontium Sulphate, $SrSO^4$, dissolves in strong sulphuric acid (sp. gr. 1.843) at 70° in the proportion of 14 pts. to 100, the solution at a higher temperature depositing tabular rhombic crystals, which at a still higher temperature are replaced by cubic and octohedral crystals (Garside, *Chem. News*, xxxi. 245).

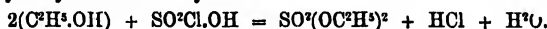
On Sulphates of *Terbium* and *Ytterbium*, see YTTRIUM METALS.

On *Vanadium Sulphates*, see VANADIUM.

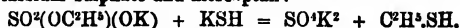
Zinc Sulphate, $ZnSO^4$.—Commercial zinc-vitriol may easily be purified from iron or manganese by adding to the boiling concentrated aqueous solution, first a small quantity of levigated zinc-white, and then a solution of zinc permanganate, till a reddish colour begins to appear (*Jahresb. f. Chem.* 1876, 1103). Zinc sulphate is completely reduced by hydrogen-potassium sulphide to white sulphide of zinc (J. Myers, *Ber.* 1873, 440).

On Double Salts of Zinc Sulphate, see p. 1876.

SULPHURIC ETHERS (Maria Mazurowska, *Ber.* viii. 332; *J. pr. Chem.* [2], xiii. 158). *Normal Ethyl Sulphate*, $SO^2 \begin{smallmatrix} \text{OC}^2H^5 \\ \text{OC}^2H^5 \end{smallmatrix}$, is obtained by the action of sulphuric hydroxychloride on ethyl alcohol:



It is a faintly yellowish, inodorous, perfectly neutral liquid, soluble in alcohol, nearly insoluble in ether, converted by water into ethylsulphuric acid. Treated with potash it yields a potassium salt, $SO^2(OC^2H^5)(OK)$, which is converted by potassium hydrosulphide into potassium sulphate and mercaptan:



The constitution $SO^2(OC^2H^5)^2$ has hitherto been assigned to the ether which Wetherill obtained in 1847 by the action of sulphuric anhydride on anhydrous ethyl alcohol (v. 624). Mazurowska, however, finds that the potassium salt of this ether does not yield mercaptan when treated with potassium hydrosulphide. She represents the ether by the formula $SO^2 \begin{smallmatrix} C^2H^5.OH \\ \text{OC}^2H^5 \end{smallmatrix}$ or $C^2H^5 \begin{smallmatrix} OH \\ \text{SO}^2.OC^2H^5 \end{smallmatrix}$, and its potassium salt by the formula $C^2H^5(OH).SO^2.OK$.

The normal ethers of methyl, propyl, butyl, and amyl are prepared in like manner by the action of sulphuric hydroxychloride on the corresponding alcohols. The *phenyl-ether*, $C^6H^5SO^4$, similarly prepared, is a thick oily liquid, which is decomposed by water yielding parphenolsulphonic acid, $C^6H^4(OH)(SO^2H)$. By heating *nitrophenol* with sulphuric hydroxychloride, decomposing the product with water, and saturating with barium carbonate, a barium salt is obtained having the composition $(C^6H^5NO^2SO^4)Ba + 2H^2O$.

Thymyl Sulphate, $SO^2(OC^6H^7H^3)^2$, has not been obtained pure, but by decomposing the product of the action of sulphuric hydroxychloride on thymol with water, and saturating with baryta-water, a barium salt is obtained having the composition $(C^6H^7H^3SO^4)^2Ba$.

Pyrosulphuric or Disulphuric Acid, $S^2O^7H^2 = 2SO^4H^2 - H^2O$. On the formation and reactions of this acid, see vii. 1149.

Thiosulphuric Acid, $H^2S^2O^3 = SO^2(OH)(SH)$ or $HO.SO.O.SH$. This acid has been found in the urine of a typhus patient (A. Strumpell, *Zeitschr. anal. Chem.* xvi. 134).

Estimation.—An indirect method of analysing a mixture of sulphites and thio-sulphates is described by J. Grossmann (*Chem. News*, xxxvii. 224). Denoting by x the quantity of iodine equivalent to the thiosulphate, by y the quantity equivalent to the sulphite, by A the total quantity of iodine used, and by B the quantity of sulphuric acid yielded by the whole after complete oxidation, then

$$x = \frac{2I}{3Na_2SO_4} \cdot B - \frac{1}{2}A; \quad y = \frac{1}{2}A - \frac{2I}{3Na_2SO_4} \cdot B$$

from which the quantities of thiosulphate x and sulphite y may be calculated by means of known coefficients.

According to Polacci (*Ber.* x. 174), thiosulphates may be separated from carbonates by gently heating the mixture with acid potassium tartrate, the carbonate alone being thereby decomposed.

Certain double thiosulphates, e.g. the lead-potassium, silver-potassium, and mercury-sodium salts, are resolved when boiled with water into sulphides and trithionates, thus: $2AgKS^2O^3 = Ag_2S + K_2S^2O^3$. The reaction, however, soon reaches a limit, and to ensure its continuation, the metallic sulphide must be separated by filtration and the boiling renewed (*W. Spring, Ber.* vii. 1157).

Ammonium thiosulphate, $(NH_4)_2S^2O^3$, is formed: 1. By combining sulphuric anhydride with ammonia and treating the resulting ammonium sulphonate with hydrogen sulphide: $SO^3 \cdot 2NH^3 + H_2S = (NH_4)_2S^2O^3$.—2. Together with small quantities of ammonium polysulphide and ammonium trithionate, when normal ammonium sulphate is heated with phosphorus pentasulphide, the thiosulphate and polysulphide subliming while the trithionate remains behind. The formation of the trithionate is probably due to a decomposition of the ammonium thiosulphate, analogous to that of the double thiosulphates above mentioned: $2(NH_4)_2S^2O^3 = (NH_4)_2S + (NH_4)_2S^3O^3$ (*Spring*).

Sodium thiosulphate, $Na_2S^2O^3$.—According to A. v. Trentinaglia (*Wien. Akad. Ber.* 1875, [2 Abth.], lxxii. 669), this salt melts at 48.09° ; and its specific heat is, for the solid state, 0.4447; for the liquid state, 0.569; latent heat of fusion 37.6 for 1 gram at 9.86° . According to T. A. Edison (*Amer. Chem.* vii. 127), it dissolves in considerable quantity in oil of turpentine, from which it almost completely removes the odour.

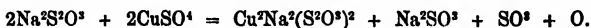
The specific gravities of the thiosulphates of barium, strontium, and calcium have been determined by T. L. Richardson (*Sill. Am. J.* [3], xiv. 281) with the following results:

BaS^2O^3, H^2O precipitated	$\left\{ \begin{array}{l} 3.4461 \text{ at } 16^\circ \\ 3.4486 \text{ at } 18^\circ \end{array} \right.$
$SrS^2O^3, 6H^2O$, in good crystals	$\left\{ \begin{array}{l} 2.1566 \text{ and } 2.1991 \text{ at } 17^\circ \\ 1.8715 \text{ at } 13.5^\circ \end{array} \right.$
$CaS^2O^3, 6H^2O$, in fine crystals	$\left\{ \begin{array}{l} 1.8728 \text{ at } 16^\circ \end{array} \right.$

Bismuth thiosulphate, $Bi_2(S^2O^3)_3$.—The double thiosulphates of bismuth and the alkali-metals, formed by mixing a slightly acid solution of a bismuth salt with sodium thiosulphate, are distinguished by their perfect solubility in water. The solutions, however, when left to themselves, change in course of time, and more quickly as they are more concentrated, sulphates being formed, together with a precipitate of bismuth sulphide. The sodium-bismuth salt dissolves also in all proportions in alcohol, whereas sodium thiosulphate is nearly insoluble in that liquid. When an alcoholic solution of potassium chloride is added to an alcoholic solution of this double salt, a copious light yellow precipitate is formed, having the composition $Bi_2(S^2O^3)_3 \cdot 3K_2S^2O^3 \cdot 2H^2O$. As no similar precipitate is formed by the chlorides of sodium, lithium, ammonium, calcium, magnesium, aluminium, manganese, iron, &c., or indeed by any metallic chlorides except those of barium, strontium, and the metals which are precipitated by hydrogen sulphide, this reaction is remarkably well adapted for the analytical separation of potassium from other metals. Further, it takes place in solutions of the nitrates as well as in those of the chlorides, but not at all, or less completely, when sulphates are present (*A. Carnot, Compt. rend.* lxxxiii. 338).

Compound of Sodio-cuprous Thiosulphate with Cupric Sulphide.—The yellow salt, to which Lenz a. Siewert assigned the formula $Na_2S^2O^3 \cdot Cu_2S^2O^3 \cdot CuS + 4H^2O$ (*Pogg. Ann.* lvi. 528), is found by Kessel (*Ber.* x. 1677, 2000; xi. 1581) to vary in composition according to temperature. When prepared at $+10^\circ$, it has a composition agreeing very nearly with Siewert's formula (atomic ratio $Na : Cu : S = 2 : 3 : 6$), but when it is prepared at -10° , the ratio is nearly $Na : Cu : S = 4 : 1 : 4$. It may be obtained with the composition given by Siewert, except as regards the amount of water, by taking care to keep the temperature down to 0° by throwing in snow during the

separation of the salt. The proportion in which the sodium thiosulphate and cupric sulphate act on one another to produce this salt are not those given by Siewert, viz. $5\text{Na}_2\text{S}_2\text{O}_3 : 3\text{CuSO}_4$, but $2\text{Na}_2\text{S}_2\text{O}_3 : \text{CuSO}_4$. That the formation of this double salt is preceded by that of another containing a larger proportion of sodium thiosulphate is inferred by Kessel from the sudden yellow coloration which takes place after the addition of a certain quantity of cupric sulphate, also from the fact that the colourless mixture gives no precipitate with soda-ley, but that after the addition of a quantity of cupric sulphate sufficient to produce the yellow coloration, soda-ley immediately produces a precipitate of cuprous oxide. Kessel has also determined the quantity of free sulphuric acid produced in the reaction, by estimating the quantity of sulphur separated from the sodium thiosulphate by the action of this free acid, and finds that 1 mol. H_2SO_4 is formed to every 2 mols. CuSO_4 , agreeing exactly with the first phase of the reaction:



The yellow salt is decomposed by cold strong hydrochloric acid, forming a white mass which contains neither sulphur nor copper chloride, is permanent when dry, but in contact with water or moist air, turns first blue and afterwards brown, with separation of copper sulphide and evolution of sulphur dioxide. It dissolves in ammonia, forming a colourless solution which slowly turns blue in contact with the air, and gives with alkalis a precipitate of cuprous oxide. By dilute mineral acids the white salt is partly dissolved, partly decomposed, with separation of copper sulphide. After deduction of admixed sodium chloride, the white salt exhibits the atomic ratio $\text{Na} : \text{Cu} : \text{S} = 3 : 1 : 3$, so that in its formation from the yellow salt, not only copper, but also sulphur, must have been eliminated.

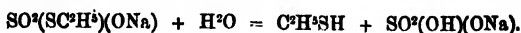
When Siewert's yellow salt is boiled with water,* it is converted into copper sulphide, sulphurous acid, and sodium sulphate, a little free sulphuric acid being probably also formed at the same time. The same decomposition is also unaccountably produced in the double salt separated at lower temperatures, which undoubtedly contains more than 1 mol. $\text{Na}_2\text{S}_2\text{O}_3$ to 1 mol. $\text{Cu}_2\text{S}_2\text{O}_3$. The white salt is also decomposed by boiling in the same manner. The supposition of Renesse (*Maandblad voor natuurwetenschap*, 3 Jahrgang, 1872-1873), that a mixture of copper and sulphur is thereby produced is inadmissible. The precipitate contains free sulphur only when the copper solution has been boiled with a large excess of sodium thiosulphate, and in this case the sulphur results from the decomposition of the sodium thiosulphate due to the action of the free sulphuric acid formed in the process.

When the yellow salt dried over sulphuric acid is drenched with hydrochloric acid, it is not converted into the white salt, but dissolves in the acid with dark brown colour, this difference of behaviour of the dried and undried salts being probably due to the different amounts of water which they contain. Alcohol precipitates from the brown solution a chocolate-coloured powder, which is resolved by heat into copper sulphide, sulphur dioxide, sulphur, and sodium sulphate, and dissolves without decomposition in water, and in dilute hydrochloric acid, but when boiled with the latter, gives off sulphur dioxide and yields a precipitate of copper sulphide. Its dilute aqueous solution is not precipitated by ammonium sulphide or by soda-ley, but the concentrated solution gives with sodium hydrate a precipitate of cuprous oxide and copper sulphide. Zinc immersed in the hydrochloric acid solution eliminates hydrogen sulphide. Ammonia does not act upon it in the cold, but throws down copper sulphide at the boiling heat, the liquid at the same time turning blue. The composition of the chocolate-coloured salt is $\text{Cu}_2\text{Na}_2(\text{S}_2\text{O}_3)_2 \cdot 2\text{CuS}$.

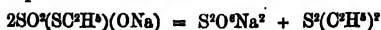
Chloropurpureocobalt thiosulphate, $(\text{Co}^2, 10\text{NH}^+)\text{Cl}^+ 2\text{S}_2\text{O}_3$, prepared by pouring a lukewarm solution of the corresponding nitrate into sodium thiosulphate, forms brownish-red orthorhombic crystals $\infty P \cdot P \infty$ with sharply defined faces (Jørgensen, *J. pr. Chem.* [2], xviii. 209).

Trimethylsulphine thiosulphate, $[(\text{CH}_3)_3\text{S}]\text{S}_2\text{O}_3$. See SULPHINES (p. 1850).

Ethyl-thiosulphuric acid, $\text{C}^2\text{H}^5\text{S}_2\text{O}_3 = \text{SO}_2(\text{SC}^2\text{H}_5)(\text{OH})$ (H. Bunte, *Ber.* vii. 646).—The sodium salt of this acid is formed by heating 1 mol. ethyl bromide for a few hours in a reflux apparatus with 1 mol. sodium thiosulphate. On evaporating to dryness at a gentle heat, and exhausting the saline mass with a little boiling alcohol, a solution is obtained which solidifies on cooling to a pulp of thin, silky, six-sided laminae, having, when recrystallised from alcohol, the composition $\text{C}^2\text{H}^5\text{S}_2\text{O}_3\text{Na}$. The neutral aqueous solution of the salt is but slightly decomposed by heating on a boiling water-bath, but on adding a small quantity of hydrochloric acid, decomposition sets in rapidly, the odour of mercaptan becomes perceptible, and sulphuric acid may be detected in the liquid:



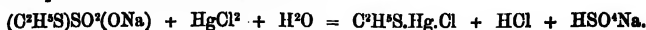
The dry sodium salt, when heated for some time at 100° , is converted into dithionate, and on distilling it in a sulphuric acid bath, sulphur dioxide is given off, and a distillate of ethyl disulphide is obtained:



and



The solution of the sodium salt yields sparingly soluble precipitates with silver nitrate, lead nitrate, and mercuric chloride. The precipitate formed with the last-mentioned reagent is quickly converted on heating into the compound $\text{C}^2\text{H}^5\text{S.Hg.Cl}$, while sulphuric acid remains in solution:



The sodium salt is readily oxidised by nitric acid, yielding sulphuric and ethylsulphonic acids.

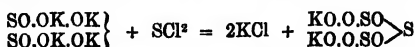
Sulphuric Peroxide, S^2O^4 . *Persulphuric acid* (Berthelot, *Ann. Chim. Phys.* [5], xiv. 345, 354; *Compt. rend.* lxxxvi. 20, 71). This oxide is formed by the action of an electric current of high tension on a mixture of equal volumes of dry sulphurous oxide and oxygen; strong sulphuric acid, under similar circumstances, does not unite either with oxygen or with ozone. The same oxide is obtained in the electrolysis of strong solutions of sulphuric acid, a circumstance which has given rise to its being confounded sometimes with hydrogen dioxide, sometimes with the imaginary substance called *antozone*. It is also formed when a solution of hydrogen dioxide is cautiously mixed with sulphuric acid containing not more than 1 mol. H^2O (not weaker than H^2SO^4), probably also in various other processes in which strong sulphuric acid is mixed with alkaline or metallic peroxides. Lastly, it may be produced directly from sulphuric oxide and oxygen; but in this case, as well as in its formation from sulphurous oxide, a large excess of oxygen is required to furnish good results.

Sulphuric peroxide, when pure, forms broad transparent flexible needles often a centimeter long, and bearing a strong resemblance to sulphuric oxide; frequently, however, it is obtained in liquid drops which solidify to indistinctly crystallised nodules. It has a considerable vapour-tension, exceeding at 10° several centimeters. At temperatures near the freezing point, it may be kept unaltered for several days, but after a while it decomposes. In aqueous solution this decomposition takes place very quickly; the solution in strong sulphuric acid is more permanent, but even in this a gradual evolution of oxygen takes place. When heated it decomposes immediately into sulphuric oxide and oxygen. In contact with the air it gives off white vapours, and gradually deliquesces to hydrogen sulphate. With baryta-water it partly decomposes, with evolution of oxygen and separation of barium sulphate, while another portion forms soluble barium persulphate, which, however, is quickly resolved into oxygen and *barium persulphate*, so that it cannot be obtained pure. The peroxide is converted by sulphurous acid into sulphuric acid, but its solution in a large quantity of strong sulphuric acid, yields, after treatment with sulphurous acid, a considerable quantity of dithionic acid.

Polythionic Acids. Michaelis (*Liebig's Annalen*, clxx. 31) represents these acids by the following constitutional formulae, based on those of sulphurous acid, $\text{SO}(\text{OH})^2$, and thiosulphuric acid, $\text{S}(\text{OH}).\text{O.S}(\text{OH})$, or—which he regards as more probable— $\text{SO}(\text{OH}).\text{O.SH}$:

Sulphurous acid	. . . $\text{SO}(\text{OH})(\text{OH})$	Thiosulphuric acid	. . . $\text{SO}(\text{OH}).\text{O.SH}$
Dithionic acid	. . . $\text{SO}(\text{OH}).\text{O}$	Tetrathionic acid.	. . . $\text{SO}(\text{OH}).\text{O.S}$
	. . . $\text{SO}(\text{OH}).\text{O}$. . . $\text{SO}(\text{OH}).\text{O.S}$
Trithionic acid	. . . $\text{SO}(\text{OH}).\text{O}$	Pentathionic acid	. . . $\text{SO}(\text{OH}).\text{O.S}$
	. . . $\text{SO}(\text{OH}).\text{O}$. . . $\text{SO}(\text{OH}).\text{O.S}$

Spring (*Ber.* vi. 1108) finds that the action of SCl^2 on potassium sulphite gives rise to trithionate and chloride of potassium, whence he assigns to trithionic acid the formula HO.O.SO.S.SO.O.OH :



When S^2Cl^2 is added by small portions to barium thiosulphate made up into a paste with a small quantity of water, sulphur separates in the first instance; and if the mass be immediately thrown on a filter, the liquid which runs through allowed to drop into sulphuric acid, and the free sulphuric acid removed by the exact quantity of barium hydrate required to combine with it, a clear liquid is obtained, exhibiting all the

reactions of pentathionic acid: hence Spring assigns to this acid the formula HO.O.SO.S.S.SO.OH .

Dithionic Acid, $\text{H}_2\text{S}_2\text{O}_6$. Several salts of this acid have been examined by H. Baker (*Chem. News*, xxxvi. 203). The *sodium salt*, $\text{Na}_2\text{S}_2\text{O}_6 + 2\text{H}_2\text{O}$, has a density of 2.175 at 11° , and forms rhombic crystals having the axial ratio $a : b : c = 0.9922 : 1 : 0.5981$, and the faces ∞P , $\bar{P} \infty$, P , \bar{P}_2 , $\infty P \infty$; prismatic from predominance of ∞P . The *silver salt*, $\text{Ag}_2\text{S}_2\text{O}_6 + 2\text{H}_2\text{O}$, forms rhombic crystals isomorphous with those of the sodium salt. $a : b : c = 0.9884 : 1 : 0.5811$. Observed faces $\bar{P} \infty$, P , ∞P , \bar{P}_2 , $\infty \bar{P} \infty$, $\infty P \infty$; habit short prismatic. The *silver-sodium salt*, $(\text{AgNa})\text{S}_2\text{O}_6 + 2\text{H}_2\text{O}$, is rhombic, with the axial ratio $0.9813 : 1 : 0.5856$, and the faces $\bar{P} \infty$, P , $\infty \bar{P} \infty$, ∞P , $\infty \bar{P} \infty$. The dome is so strongly developed that the crystals appear horizontally prismatic (Baker). The *barium salt*, $\text{BaS}_2\text{O}_6 + 2\text{H}_2\text{O}$, has a density of 4.536 at 13.5° . Its saturated solution boils at 102° , and 1 pt. of the salt dissolves in 0.994 pts. water at this temperature; according to an older statement by Heeren (*Ann. Phys. Chem.*, vii. 172), 1 pt. of the salt dissolves in 1.1 pt. of boiling water. The *calcium salt*, $\text{CaS}_2\text{O}_6 + 4\text{H}_2\text{O}$, has a density of 2.176 at 11° . From the corrosion-figures of these two salts, Baumhauer (*Zeitschr. Kryst. i.* 54) infers that they crystallise in rhombohedral-hemihedral forms, and not in tetartohedral forms, as might be supposed from their optical rotatory power. The *magnesium salt*, $\text{MgS}_2\text{O}_6 + 6\text{H}_2\text{O}$, crystallises in oblique prisms dissolving in 0.692 pt. water at 17° . The *nickel salt*, $\text{NiS}_2\text{O}_6 + 6\text{H}_2\text{O}$, dissolves in 0.897 pt. water at 12° .

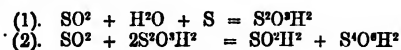
Hypovanadic dithionate is prepared by precipitating a solution of the barium salt with the requisite quantity of hypovanadic sulphate, and evaporating the blue filtrate in a vacuum. It then separates in crystals, which, however, always retain a small quantity of the sulphate (E. J. Bevan, *Chem. News*, xxxvii. 294).

Chloropurpureocobalt dithionate, $(\text{Co}^2, 10\text{NH}^3)\text{Cl}^2, \text{S}_2\text{O}_6^{12}$, obtained by pouring a lukewarm solution of the corresponding nitrate into sodium dithionate, crystallises in shining rectangular prisms (Jørgensen, *J. pr. Chem.* [2], xviii. 209).

Aniline dithionate, $(\text{C}^6\text{H}^3\text{N})^2\text{H}_2\text{S}_2\text{O}_6$, is obtained in fine long needles by decomposing aniline sulphate with barium dithionate. It is a moderately stable compound, dissolving without decomposition in water and in alcohol. 100 pts. water at 16° dissolve 7.89 pts. of this salt (Bevan).

Trithionic Acid, $\text{H}_2\text{S}_3\text{O}_6$. On the formation of the ammonium salt of this acid by heating ammonium sulphate with phosphorus pentasulphide, see p. 1879. It is also formed when sulphur sulphodichloride, S^2Cl_2 , is added by drops to a solution of normal potassium sulphite. The *potassium salt*, $\text{K}_2\text{S}_3\text{O}_6$, prepared by the action of sulphurous acid on a saturated solution of potassium thiosulphate, crystallises in orthorhombic needles. $a : b : c = 0.3586 : 1 : 0.4204$. Observed faces ∞P , ∞P_2 , $\infty P \infty$, $\infty \bar{P} \infty$, $\bar{P} \infty$. An attempt to prepare the sodium salt by a similar process yielded nothing but crystals of the thiosulphate (Baker, *loc. cit.*) When a concentrated solution of potassium trithionate and sulphite is heated with solution of cupric sulphate, the liquid becomes colourless, and on cooling deposits a double salt, $\text{Cu}^2\text{S}_3\text{O}_6, \text{K}_2\text{S}_3\text{O}_6 + \text{H}_2\text{O}$, in white needles having a silky lustre (Spring, *Ber.* vi. 1108). *Thallium trithionate*, $\text{Tl}_2\text{S}_3\text{O}_6$, separates, on evaporating a solution of thallium carbonate in trithionic acid, in colourless needle-shaped crystals isomorphous with the potassium salt. It decomposes slowly at ordinary temperatures, quickly when heated, and is therefore difficult to obtain free from sulphate.

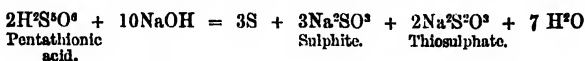
Tetrathionic Acid, $\text{H}_2\text{S}_4\text{O}_6$. According to Spring (*Bull. Belg.* [2], xlv. No. 5, May, 1878), the production of this acid from sulphurous oxide and hydrogen sulphide is due to the formation of thiosulphuric acid by the action of sulphurous acid upon sulphur, and its subsequent oxidation by the excess of sulphurous oxide present, as represented by the equations:



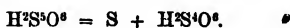
The correctness of these equations is shown by the fact that tetrathionic acid may be obtained by the action of sulphurous acid on flowers of sulphur, and that the hypsulphurous acid, which should be formed according to the second equation, may be actually detected by its strong reducing action on solution of indigo.

Pentathionic Acid, $\text{H}_2\text{S}_5\text{O}_6$. The existence of this acid, which, according to Wackenroder, is produced by passing hydrogen sulphide in excess into a saturated aqueous solution of sulphurous acid (v. 642), has been called in question by M. W. Spring (*Bull. Acad. Belg.* [2], No. 5, Mai, 1878), who states, as the result of his own experiments, that the acid solution thus produced contains, not pentathionic acid, but

a mixture of tetrathionic and hyposulphurous acids; that it is not decomposed by alkaline hydrates (as stated by Wackenroder, who cites this decomposition, with precipitation of sulphur, as a test for distinguishing pentathionic from tetrathionic acid), but that, on addition of the alkali, a tetrathionate is formed, without precipitation of sulphur. Stingl & Morawski, on the other hand (*J. pr. Chem.* [2], xx. 76), find, both by qualitative and quantitative experiments, that Wackenroder's solution contains an acid richer in sulphur than tetrathionic acid; and the same conclusion results from the recent experiments of Takamatsu & Watson Smith (*Chem. Soc. J.* xxxvii. 592), who also point out that the acid contained in Wackenroder's solution is clearly distinguished from tetrathionic and all the other polythionic acids by the fact that it is decomposed, with separation of sulphur, by alkaline and earthy hydrates, by alkaline carbonates, and gradually even by earthy carbonates, its salts being indeed very unstable, though the acid itself is stable. The sulphur thus precipitated is redissolved by the alkali on boiling, and even on standing for some time at ordinary temperatures. The action of alkalis on pentathionic acid in aqueous solution may be represented by the equation:



In an ether-alcoholic solution a different reaction takes place, resulting in the formation of tetrathionic acid:



In this case, also, sulphur is separated, but in smaller quantity, and it is immediately taken up by the alcohol: hence the mistake made by Spring, who treated a mixture of Wackenroder's solution with alcohol and ether, and then added a solution of caustic soda, and finding that no sulphur was precipitated, and that the solution contained tetrathionic acid, concluded that the latter acid was the immediate product of Wackenroder's reaction; whereas it now appears from the experiments of Takamatsu & Smith that the addition of the alkali does really give rise to a separation of sulphur, but that the sulphur is immediately dissolved by the ether-alcohol. When a small quantity of the Wackenroder solution was treated in a test-tube with strong alcohol, then with ether, and a few drops of caustic soda-solution were added to the resulting clear liquid, an immediate turbidity was produced in the upper alkaline layer, which was formed for an instant, evidently in consequence of separation of sulphur, but as this alkaline layer sank through the liquid and mixed with the subnatant ether-alcoholic solution, the precipitate quickly disappeared. On adding more caustic soda, a further precipitate was formed, but this also quickly disappeared on agitation.

Tetrathionic and pentathionic acids may be prepared synthetically by acting upon lead thiosulphate with a solution of iodine in hydriodic acid, a moderately strong solution giving rise to tetrathionic, and a solution as strong as can be obtained producing pentathionic acid. The formation of the latter is represented by the equation:



Reactions of the Polythionic acids.—The following table (p. 1884) exhibits a comparative view of the reactions of these acids with various tests.

SUPERPHOSPHATES. See PHOSPHATES (p. 1596).

SYENITE. This rock from Biella has been analysed by A. Cossa (*Jahrb. f. Min.* 1876, 874) with the following result:

SiO ²	P ² O ⁵	TiO ²	Al ² O ³	Fe ² O ³	FeO	CaO	MgO	K ² O	Na ² O
59.37	0.58	0.26	17.92	6.77	2.02	4.16	1.83	6.68	1.24 = 100.83

Also 0.38 loss by ignition, water, and CO².

From these analytical data, and from the specific gravity of the rock (2.710), compared with that of orthoclase crystals (2.573), and that of hornblende crystals (3.157), Cossa calculates 76.5 per cent. orthoclase, and 23.5 per cent. hornblende, as constituents of the rock. Kenngott, however (*Jahrbuch*, 1877, 169), objects to this conclusion.

Syenite granites.—(1). From Ravenswood in Queensland, in which plagioclase, quartz, mica, and hornblende were perceptible (Daintree, *Geol. Soc. Qu. J.* xxviii. 271).—2 and 3. Syenite-granites from Minnesota, including porphyritic mixtures of quartz, orthoclase, oligoclase, and small quantities of hornblende, biotite, apatite, and magnetic or titanite iron ore. The hornblendes appear to enclose an augitic nucleus. 3. From Sauk Rapids, medium to coarse-grained; 3. From Watab, porphyritic (Streng & Kloos, *Jahrb. f. Min.* 1877, 225).

Distinguishing Reactions of the Polythionic Acids.

Reagents	Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$	Trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$	Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$	Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$
Caustic potash.	No precipitate.	No precipitate.	No precipitate.	Immediate precipitate of sulphur, redissolving gradually on standing, if not in much excess and coagulated.
Dilute hydrochloric acid.	No action.	Evolution of SO_2 , and precipitate of S.	No action.	No action.
Mercurous nitrate.	No precipitate.	Immediate black precipitate, becoming white on standing.	Yellow precipitate, gradually darkening.	At first yellow precipitate, turning white with excess of reagent on standing.
Silver nitrate.	No precipitate.	Yellow precipitate, soon becoming black.	Yellow precipitate, soon turning black, and also on adding ammonia.	Yellow precipitate, gradually darkening; black on adding ammonia.
Ammoniacal silver nitrate.	—	No brown coloration, even on standing. On warming, Ag_2S formed.	No dark or brown coloration, even on standing, <i>unless warmed</i> .	Almost immediate brown coloration, becoming black on warming.
Mercuric cyanide.	No precipitate.	—	At first yellow precipitate; turns black on warming, with evolution of HCN .	At first yellow precipitate, gradually turning on heating, with evolution of HCN .
Mercuric chloride.	No precipitate.	Yellow precipitate, becoming white with excess of reagent.	On warming, white precipitate.	On warming, whitish yellow precipitate.
Potassium sulphhydrate solution.	—	—	White precipitate of sulphur.	White precipitate of sulphur.
Dilute solution of potassium permanganate.	One drop, immediate brown precipitate.	One drop, immediate brown precipitate, even in presence of dilute SO_2H_2 .	Decolorised, without addition of dilute sulphuric acid.	Decolorised, without addition of dilute sulphuric acid.

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	CaO	K ² O	Na ² O	H ² O	
(1).	60.07	21.18	—	5.53	2.07	4.83	2.12	2.23	1.96	= 99.90
(2).	67.70	16.11	2.47	2.29	1.11	2.89	4.47	3.64	0.83	= 101.51
(3).	70.05	15.04	1.70	1.09	0.82	1.97	5.09	4.77	0.81	= 101.24

On *Syenite-porphyrries* from South Norway, see Liebisch (*Jahrb. f. Min.* 1876, 412; *Chem. Soc. J.* xxxvi. 362).

SYNPOORITE. See JETPOORITE (p. 1142).

SYLVANITE. See TELLURIUM MINERALS.

SYLVESTRENE, C¹⁰H¹⁶. A terpene occurring, together with australene, in Swedish wood-tar from *Pinus sylvestris*. It is a colourless liquid, boiling between 173° and 175°, having a specific gravity of 0.8612 at 16°, and a rotation-coefficient of +19.5° for sodium light. The dihydrochloride, obtained by passing hydrogen-chloride into an ethereal solution of sylvestrene, crystallises in broad, flat, shining needles, or in bar-shaped crystals melting at 72°–73°; it is somewhat strongly attacked by water at 100°, and completely decomposed by alcoholic potash with formation of potassium chloride. The last reaction also yields an oil which has an odour of polargonium, and is likewise produced by treating the dihydrochloride with aniline; it appears to be a torpinol-like substance, 4C¹⁰H¹⁶ + H²O, and is reconverted by hydrogen chloride into the dihydrochloride (Atterberg, *Ber.* x. 1202).

SYLVIN. Fibrous sylvin from Kalusz has been found by Niedzwiedzki (*Min. Mitt.* 1877, 95) to contain 60 to 80 per cent. KCl, together with NaCl. Nodules of anhydrite 3 to 4 cm. in diameter were imbedded in it.

SYMPLOCOS. Lotur-bark, from *Symplocos racemosa*, a tree indigenous in India, contains three alkaloids, loturine, colloturine, and loturidine. *Loturine* may be easily obtained in crystals from its solution in acetone, ether, or alcohol, and is characterised by the intense blue-violet fluorescence of its solutions in dilute acids. *Colloturine* crystallises in long shining prisms, terminated at both ends by pyramids, and sublimates at 234°. Its solutions in dilute acids likewise exhibit a blue-violet fluorescence. *Loturidine* is amorphous; its solutions in dilute acids exhibit a blue-violet fluorescence, which becomes especially conspicuous when the solution is strongly diluted.

SYNANTHRENE. A constituent of crude anthracene, probably having the formula C¹¹H¹⁰. It forms a dibromo-derivative, C¹¹H⁸Br², which crystallises in light yellow microscopic needles, sublimates undecomposed, melts at 175°, is more soluble than dibromanthracene in benzene and tar-oils, moderately soluble in hot alcohol. By boiling with alcoholic potash it is gradually converted into a viscid resin, which is precipitable by water, but does not yield any crystalline constituent (Zeidler, *Wien. Akad. Ber.* [2 Abth.], lxxvi. 231).

SYNANTHROSE. On the occurrence of this kind of sugar in rye, see p. 1768.

SZABOITE. A mineral occurring, together with tridymite and pseudobrookite, in clefts and cavities of the andesite of the Aranyer Berg in Transylvania. Crystal triclinic, exhibiting the faces $\{P\}$; $2\{P'\}$; ∞ ; OP . Colour hair-brown to hyacinth-red. Analysis gave 52.35 per cent. SiO², 44.70 Fe²O³, and 3.12 CaO, with 0.4 loss on ignition, leading to the formula Fe²²Ca²Si³⁵O¹⁰⁵ = 11Fe²Si³O⁹ + 2CaSiO³ (A. Koch, *Jahrb. f. Min.* 1878, 652; *Zeitschr. Kryst.* iii. 307).

SZMIKITE. A reddish-white to rose-red mineral, occurring in stalactitic nodules in an abandoned mine at Felsobanya, and agreeing, according to the analyses of Schrauf (A.) and Dietrich (B.), with the formula MnSO⁴ + H²O (C.) Sp. gr. = 3.15.

	SO ³	MnO	H ² O
(A.)	47.43	41.78	10.92 = 100.13
(B.)	47.11	41.61	11.19 = 99.91
(C.)	47.34	42.01	10.65 = 100

(J. v. Schröckinger, *Jahrb. f. Min.* 1877, 729).

T.

TACAMAHACIN. A crystallised body contained in the yellow resin of the Tacamahac or Balsam poplar. It is insoluble in ether, aqueous alcohol, ammonia, and potash, slightly soluble in hot absolute alcohol, not altered by nitric acid, but dissolved with violet coloration by sulphuric acid (Batka, *Arch. Pharm.* [3], vi. 111).

TACHYLITE. The following analyses of this mineral from the basalt of the Rossberg are given by T. Petersen (*Jahrb. f. Min.* 1873, 385). A. Fresh; sp. gr. 2.624. B. Decomposed.

	SiO ²	TiO ²	Al ² O ³	Fe ² O ³ , FeO	MgO	CaO	Na ² O	K ² O	H ² O
A.	66.42	0.31	13.07	3.66	1.30	1.19	6.09	7.36	0.75 = 100.13
B.	62.43		17.12	1.82	0.68	0.30	6.19	7.95	2.81 = 99.30

TAGETES. The flowers of the common marigold (*Tagetes patula*), and other species of the same genus, contain a crystallisable substance, quercetagetin, having the composition C²⁷H²⁶O¹³ + 4H²O (p. 1732).

TALC. Pseudomorphs of talc after pectolite, occurring in the calcite-veins of the 'Trapp' of Bergen Hill, Hoboken, New Jersey, have been described and analysed by A. R. Leeds (*Sill. Am. J.* [3], vi. 23).

SiO ²	Al ² O ³	MgO	FeO	MnO	CaO	H ² O	Sp. gr.
60.54	1.06	26.46	0.70	0.55	1.19	9.52 = 100.02	2.565
60.57	0.98	26.67	0.74	0.76	1.65	9.07 = 100.44	

TANNINS. Ordinary tannin, or the tannin of nut-galls, C³⁴H²²O²², appears, from the experiments of H. Schiff, to be most probably a glucoside of digallic acid, C¹⁴H¹⁰O⁸ (p. 646); see also *Liebig's Annalen*, clxxv. 165. P. Freda (*Gazz. chim. ital.* 1878, 9) has endeavoured to settle the question as to whether this tannin is a glucoside, by means of fermentation experiments. For this purpose he used: 1. A solution of commercial tannic acid mixed with a few drops of acetic acid; 2. A solution neutralised with potash, and then slightly acidulated with acetic acid; 3. Solutions prepared in like manner, and mixed with various quantities of glucose; 4. A solution of tannic acid which had been boiled for some time with sulphuric acid, then neutralised with marble, filtered, evaporated to dryness, and redissolved in water. These solutions were treated with fresh beer-yeast, and left to ferment under the usual conditions. In 1 and 2 no fermentation took place; in 3 and 4 brisk fermentation. Parallel experiments with amygdalin and salicin yielded the same result. From these results Freda infers that gallotannic acid is really a glucoside, and not merely a mixture of tannic acid and glucose, since such a mixture would have fermented in contact with the yeast as the added glucose did. Schiff (*Gazz.* 1878, 87) does not regard Freda's experiments as conclusive, but nevertheless adheres to his opinion that the unaltered tannin of nut-galls is a very easily decomposable glucoside of digallic acid.

Artificial Formation (?)—When citric acid is gently heated with phosphorus oxychloride, a violent action takes place, and the residue left after the excess of the oxychloride has been partly distilled off, yields to ether a coloured flocculent substance, which, after repeated solution in water and precipitation with hydrochloric acid (the colouring matter going down with it), gives by analysis 53.5 per cent. C. and 2.9 H, [the formula C³⁴H²⁰O²² requires 51.8 C. and 3.6 H], and after drying dissolves slowly and abundantly in water, yielding a solution which exhibits all the reactions of tannic acid, except that it acts less strongly on iodide of starch (Schiff, *Liebig's Annalen*, clxxii. 359).

Estimation.—To estimate the amount of tannin in any given tanning material (galls, sumach, &c.), J. Löwenthal (*Zeitschr. anal. Chem.* xvi. 33; *Chem. Soc. J.* xxxi. 745) first titrates a measured volume of the extract with permanganate solution, using indigo as an indicator, so as to ascertain its permanganate value; then precipitates the tannin from another equal portion of the extract by means of a solution of gelatin saturated with common salt; and titrates the filtrate in the same manner: the difference of the two titrations determines the quantity of tannin in the solution.

On the estimation of Tannin in *Tea* by this method, see Estcourt (*Chem. News*, xxix. 109; *Chem. Soc. J.* xxvii. 712).

On an older method proposed by Löwenthal, see *J. pr. Chem.* lxxxi. 150; *Jahresb. f. Chem.* 1860, 680. Observations thereon, by J. M. Merrick (*Amer. Chem.* 1873, iii. 324; iv. 15, 202; *Jahresb. f. Chem.* 1873, 971).

Prud'homme (*Bull. Soc. Chim.* [2], xxi. 169) estimates tannin by oxidation with bleaching-powder, using aniline-green as indicator. The bleaching liquid is first standardised against the colouring matter, and afterwards against successive portions of a standard tannin solution, to which small quantities (say 10 c.c.) of the aniline colour have been added. On deducting the volume of chloride of lime corresponding with the known quantity of colouring-matter, the remainder indicates the quantity of tannic acid present. Solutions of gallic and pyrogallic acids may be examined in a similar manner. To apply the method to the valuation of commercial tannins, a known weight of pure tannin is added to a known volume of methyl-green, and the solution made up to a certain volume; the precipitated lake is filtered off; and the residuary colouring matter estimated by the chloride of lime solution. A similar treatment applied to the same weight of the commercial tannin will show the ratio of quality existing between the two tannins.

E. Schmidt (*Bull. Soc. Chim.* [2], xxi. 256) estimates tannin volumetrically by a modification of a method proposed by Pribram (*ibid.* vii. 496; *Jahresb. f. Chem.* 1866, 821), which depends on the precipitation of the tannin by lead acetate. 50 grams of neutral lead acetate are dissolved in 400 g. alcohol, and the solution is made up to a litre with distilled water. A second solution is prepared by dissolving 1 g. tannin in 40 g. alcohol, and diluted with water to 100 c.c.; 10 c.c. of the tannin solution is then mixed with 20 c.c. water; the whole is heated to 60°; and the lead-liquor is poured into the hot solution as long as a precipitate is formed, a solution of potassium iodide being used to indicate excess of lead. To prepare the solution of the tanning material under examination, a weighed quantity of the coarsely pulverised bark is exhausted with water at 50°-60°; the filtrate is evaporated to dryness; the residual extract is dissolved in 40 g. alcohol of 92 per cent.; and the solution is diluted with water to 100 c.c. This treatment effects the separation of resinous and gummy constituents, the tannic acid then remaining contaminated only with soluble organic salts and extractive matters. As, however, some of these foreign matters are, under certain circumstances, likewise precipitated by lead acetate, Schmidt endeavours to estimate them approximately by treating equal quantities of the impure tannin solution, and a solution of pure tannin containing a somewhat smaller amount of tannic acid, under exactly similar conditions and in similar vessels, with animal charcoal, which absorbs part of the tannic acid, but not the foreign substances. Assuming, then, that equal quantities of tannic acid are absorbed in the two cases, the excess of lead acetate solution used to precipitate the impure tannin over that required for an equal quantity of the pure tannin solution will give approximately the amount of the foreign constituents.

Gerland (*Zeitschr. anal. Chem.* ii. 419) estimates tannin volumetrically by means of a solution of tartar-emetic containing 2.611 g. of the dried salt in a litre. This solution (1 c.c. of which corresponds to 0.005 g. tannic acid) produces in neutral or slightly acid solutions of tannic acid a precipitate of antimonious tannate, which quickly settles down on addition of sal-ammoniac. A slight modification of this method is proposed by Richards a. Palmer (*Sill. Am. J.* [3], xvi. 196, 361), which consists in titrating the tannin solution containing at least 0.1-0.3 g. tannic acid, with solution of tartar-emetic containing 6.73 g. of the dried salt $C_2H_4KSbO_7$ in the litre, the end of the reaction being indicated by ammonium sulphide, after the tannate has been separated by addition of ammonium acetate.

A. Gautier (*Zeitschr. anal. Chem.* xvii. 222) estimates tannic acid in wine by agitating 100-200 c.c. of the wine with 1-2 g. recently precipitated cupric carbonate, then adding an equal volume of alcohol, and leaving the mixture at rest for twelve to twenty hours. The tannic acid then separates in the form of an insoluble copper-compound, whilst the colouring matter of the wine (*anotannin*) remains in solution, probably also in combination with copper.

For the estimation of tannin in the must of the grape and in wine, Pavesi a. Rotondi (*Gazz. chim. ital.* 1874, 192) adopt a modification of a method originally proposed by Fleck, which consists in precipitating the tannin with a solution of cupric acetate. A neutral solution of this salt, however, also precipitates gallic acid, but an ammoniacal solution of cupric acetate precipitates only the tannin, and has no action on any of the other constituents of the wine. The amount of tannin can be ascertained by estimating either the copper remaining in solution, or that contained in the precipitate. The process is simple and gives accurate results.

Carpene (*ibid.* 1875, 120) separates the tannin from the other constituents of wine by means of an ammoniacal solution of zinc acetate containing a large excess of ammonia, which forms with tannin a tannate of zinc quite insoluble in water, in

ammonia, and in an excess of the reagent itself, and no precipitate with alcohol, malic acid, tartaric acid, potassium bitartrate, calcium tartrate, glycerol, gelatin, albumin, or the ferrous and ferric salts of organic acids. With gallic acid, succinic acid, glucose, and aluminium salts, it forms precipitates soluble in excess of the reagent and in ammonia. Lastly, it forms a violet precipitate with a solution of cœnocyantin prepared according to Macagno's method. This, however, does not interfere with its use in the method of analysis under consideration.

On treating the wine with an excess of this reagent, a precipitate is formed consisting of zinc tannate mixed with a small quantity of colouring matter. The wine is heated nearly to boiling to agglomerate the flocculent precipitate, and the precipitate after cooling is washed on a filter with a small quantity of boiling water, which removes the adhering colouring matter. On dissolving the precipitate in dilute sulphuric acid, a solution is obtained containing all the tannin of the wine, and having a very faint red tint, due to minute traces of cœnocyantin, which compensate for the slight loss of tannin incurred in the manipulations. In this acid liquid the quantity of tannic acid is determined volumetrically with a millinormal solution of potassium permanganate, each cubic centimeter of which is equivalent to 0.00760 gram of tannic acid. The examples given of the application of this method to several wines show that it is capable of giving very exact results.

A method of estimating tannin by filtration through *skin*, which absorbs the tannin and allows the other soluble substances to pass through, was proposed by Hammer (*J. pr. Chem.* lxxxi. 159; *Jahresh. f. Chem.* 1860, 679), and has more recently been adopted with some modifications by Muntz a. Ramsbacher (*Dingl. pol. J.* ccxiv. 74; *Chem. Soc. J.* xxvii. 1183). According to R. Procter, however (*Chem. News*, xxxiii. 245), this method cannot give exact results, inasmuch as a solution containing only 1 per cent. tannin can pass through skin 2 or 3 mm. thick, and, moreover, skin in general is capable of fixing only a certain quantity of tannin.

Hop-tannin. The tannin of hops is amorphous; does not precipitate a solution of gelatin; is slightly soluble in cold water, easily in hot water; also in alcohol and ethyl acetate; insoluble in ethyl oxide. It is easily alterable; turns red, and gives off water at 100°, and then, like gallotannic acid, precipitates a solution of gelatin. Hop-tannin also resembles gallotannin in being converted, with elimination of water, into a phlobaphene having the composition $C^{26}H^{16}O^{22}$, when its aqueous solution is heated to 120°; this phlobaphene exists also ready formed in hop-cones, and may easily be prepared therefrom (C. Etti, *Dingl. pol. J.* cccxxviii. 254; *Chem. Soc. J.* xxxiv. 797).

Oak-tannins. The amount of tannin in oak-branches more than a year old remains nearly constant from March till the end of October; the buds contain a much larger proportion than the branches. In the young shoots the amount of tannin increases considerably from July onwards, but decreases in winter, probably in consequence of internal respiration. The proportion of tannin in the leaves is very considerable, and appears to be determined by the individuality of the tree, leaves of different trees exhibiting considerable diversity in their proportion of tannin. The tannin of the leaves is identical with that of the bark; the leaves also contain ellagic acid. The composition of oak-bark tannin may be represented by the formula $C^{22}H^{20}O^{11}$; that of oak-red by $C^{14}H^{10}O^6$; and the relations of the latter to ellagic acid and to gallotannic acid by the equations $C^{14}H^{10}O^6 + O^2 = C^{14}H^{10}O^8$ (gallotannic acid); $C^{14}H^{10}O^6 + O^4 = 2H^2O + C^{14}H^8O^8$ (ellagic acid) (J. Oser, *Wien. Akad. Ber.* [2 Abth.], lxxii. 165).

Strawberry-tannin, or Fragarianin. The root of the strawberry (*Fragaria vesca*) contains, according to Phipson, a tannic acid analogous to quinotannic acid, which he designates as *Fragarianin*. This tannin is resolved, by boiling with hydrochloric acid, into sugar and a red amorphous body called *Fragarin*, which is soluble in water, alcohol, and ether, and dissolves, with fine red colour, in potash-ley. Strong sulphuric acid dissolves fragarin; nitric acid converts it into a yellow nitro-compound different from picric acid; with potassium chlorate and hydrochloric acid it yields a yellow chlorinated product. When heated, it yields a small quantity of catechol, and when fused with potassium hydroxide, a small quantity of protocatechuic acid. Strawberry-root also contains bodies resembling quinovin and quinovic acid, together with a small quantity of ordinary tannin.

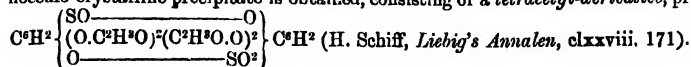
On *Divi-divi Tannin*, see ELLAGITANNIC ACID (p. 731).

On the presence of Tannin in various species of *Willow*, see Johanson (*Arch. Pharm.* [3], xiii. 103; *Chem. Soc. J.* xxxvi. 160).

Sulphotannic Acid, $C^{12}H^{10}S^2O^{11}$ (vii. 1125). *Acetyl-derivatives.*—*Pentacetyl-sulphotannic acid, C^6H^2* $\left\{ \begin{array}{l} (O.C^2H^3O)(C^2H^3O.O)^2 \\ SO^2.OH \\ SO^2 \text{ ————— } O \end{array} \right\} C^6H^2$, is obtained by gradually adding

sulphotannic acid to a mixture of equal volumes of glacial acetic acid and acetic anhydride, in which it dissolves at ordinary temperatures. The solution is heated for about two hours in a reflux apparatus; the excess of acid and anhydride distilled off; the residue mixed with a large quantity of ether; and the crystalline precipitate is washed with cold and dissolved in boiling alcohol. On cooling, the pentacetyl-compound separates in small orange-coloured crystals insoluble in water, but soluble in caustic alkalis.

When sulphotannic acid is added in like manner to pure acetic anhydride, a flocculo-crystalline precipitate is obtained, consisting of a *tetracetyl-derivative*, probably



TANTALUM. Atomic Weight 182. A nitride of tantalum, Ta^3N_5 , is produced by heating tantalum chloride, $TaCl_5$, in a current of ammonia-gas at a temperature a little above the subliming point of sal-ammoniac. It is an amorphous, ochre-yellow mass, which, when heated to whiteness in a stream of perfectly dry ammonia-gas, gives off nitrogen, and is converted into a black amorphous mass of the mononitride TaN .

A carbonitride, $10\text{TaC}\cdot\text{Ta}_3\text{N}$, is obtained, like the carbonitrides of niobium (p. 1393), by heating tantalum oxide, Ta_2O_5 , with sodium carbonate and charcoal at about the temperature of melting cast-iron. The product has a fine brass-yellow colour (A. Joly, *Compt. rend.* lxxxii, 1195).

Tantalates.—Tantalic acid forms with most bases four series of salts analogous in composition to the niobates described by Joly (p. 1393), viz.:



When tantalic acid is dissolved in a hot concentrated solution of ammonium fluoride, the salt $\text{TaOF}_3 \cdot 3\text{NH}_4\text{F}$ crystallises on cooling in regular octohedrons. The corresponding *potassium salt* has not been obtained pure (Joly, *Compt. rend.* lxxxi. 1266).

A tantalate occurring, together with beryl, columbite, samarskite, and garnet, in Yancey County, North Carolina, was found by G. Koenig (*Jahrb. f. Min.* 1876, 867) to contain:

Ta ₂ O ₅	FeO	MnO	MgO	
76.60	14.07	0.50	7.70	= 98.87

Kenig refers it to the species tantalite, but Kennigott shows (*ibid.* 1877, 168) that its composition does not agree with the formulæ of that species.

Tantalite occurring in lumps of the size of peas, and of sp. gr. 7.305-7.401, in the decomposed granite of Cousa County, Alabama, has been analysed J. L. Smith (*Sill. Am. J.* [2], xv, 203), with the following results:

Ta ₂ O ₅	WO ₃	ZnO	MnO	FeO	CuO	
79.55	1.10	0.87	3.72	13.51	0.89	= 99.74

Smith regards the locality above mentioned as the first at which tantalite has been found in North America, and agrees with Kenngott in doubting the correctness of K  nig's view of the constitution of the mineral from North Carolina.

TAR. According to Liebermann a. Burg (*Ber.* xi. 723), the vapour of lignite-tar, when passed through a red-hot tube filled with porous substances, is converted, with copious evolution of gas (56-63 p. c.), into a mixture resembling coal-tar, and, like the latter, containing about 4 per cent. benzene and toluene, together with 0.9 per cent. crude anthracene. The largest quantity of gas was produced with empty tubes; the smallest with tubes filled with charcoal. When the oils thus obtained, or those produced from coal-tar itself, are passed through a red-hot tube, they experience a much smaller loss in weight, from 77-90 per cent. of the original quantity being recovered. Petroleum and vulcan oil similarly treated yield large quantities of gas and benzene, but no anthracene.

Salzmänn a. Wichelhaus (*Ber.* xi. 802) also find that when lignite-tar oil is decomposed by red-hot charcoal, 4 per cent. of an oil is obtained, which boils at 120°, and yields nitrobenzene. The same chemists find that the formation of benzene from lignite-tar is always attended with separation of carbon, and that abstraction of hydrogen, which may be effected by the admixture of oxygen with the oil-vapours as they pass over the red-hot charcoal, does not produce any essential alteration in the result of this decomposition.

Lotny (*Ber.* xi. 1210) finds that when the vapours of hydrocarbons of the fatty series—especially the residues of Baku petroleum (b. p. 270°) are passed several times through a red-hot retort 7 feet long and 1 foot wide filled with charcoal, they yield a tar having a sp. gr. of 1.307. This tar yielded on distillation 2.3 per cent.

water, 4.6 benzene, 5.2 toluene and its homologues, together with 35.4 naphthalene and unaltered petroleum. Lastly, the residue boiling above 340° was found to contain—together with petroleum—considerable quantities of phenanthrene and anthracene. Still more complete is the decomposition when narrow tubes are employed. The distillation-products of natural asphalt and resinous shales are also decomposed in a similar manner under these conditions. Atterberg (*Ber.* xi. 1222), by subjecting pine-wood tar—the heavy tar-oil of Swedish wood-oil manufactories—to the action of red-hot coke in iron retorts, obtained, at commencing redness, the same products as those which are formed under these circumstances from lignite-tar and petroleum; they contained 0.3 per cent. anthracene, together with benzene, toluene, and phenol. When the coke was heated to bright redness, the product contained relatively more benzene and naphthalene, but less phenol.

TARTARIC ACID, $C^4H^4O^6$. The following process for the preparation of this acid is recommended by F. Dietrich (*Jahresb. f. Chem.* 1878, 1136). Tartar is subjected to the action of calcium carbonate in presence of water at a high temperature and under pressure, whereupon, as the carbonic acid cannot escape, the two salts act on one another so as to form potassium bicarbonate and calcium tartrate, which is decomposed in the usual way. The quantity of water is regulated so as to form a saturated solution of potassium bicarbonate.

On the Optical Rotatory Power of Tartaric Acid and its Salts, see LIGHT (pp. 1217-1219).

Solubility.—According to Bourgoin (*Ann. Chim. Phys.* [5], xiii. 400), 100 pts. by weight of alcohol and ether at 15° dissolve the following quantities of tartaric acid:

Ether	Absolute alcohol	Alcohol of 90°
0.400	25.604	41.135

Distinction between Tartaric and Citric Acids.—These two acids may be distinguished by their reaction with *potassium dichromate*, a cold saturated solution of this salt giving with tartaric acid a dark brown colour, with evolution of carbon dioxide, whereas on citric acid it acts but slowly, producing only a light brown colour. If 1 gram of powdered citric acid be added to 10 c.c. of the cold-saturated dichromate solution, the orange colour of the liquid remains unchanged after ten minutes if no tartaric acid is present; whereas 5 per cent. of that acid will produce a dark brown, and 1 per cent. a coffee-brown colour (Cailletet, *Chem. Centr.* 1879, 14).

According to A. H. Allen (*Zeitschr. anal. Chem.* 1877, 251), tartaric and citric acid may be separated in alcoholic solution by means of potassium acetate, also dissolved in alcohol, which throws down a precipitate of acid potassium tartrate.

Estimation.—To determine the amount of tartaric acid in crude tartar and similar substances, A. Scheurer-Kestner (*Compt. rend.* lxxxvi. 1024) dissolves the sample in hydrochloric acid, neutralises the filtrate with soda, and precipitates with calcium chloride. The washed precipitate is converted by ignition into carbonate, which is then titrated.

See also Warington (*Chem. Soc. J.* xxviii. 959-981).

On the Estimation of Tartaric Acid and its separation from Citric Acid in Solutions, Fruit-Juices, and Insoluble Substances, see CITRIC ACID (p. 508 of this volume).

On the Conversion of Dextrotartaric Acid into Racemic and Inactive Tartaric or Mesotartaric Acid, see Jungfleisch (vii. 1147).

Tartrates. *Ferrous Tartrate*, $C^4H^4FeO^6$.—According to C. Méhu (*N. Jahrb. Pharm.* xl. 257), the directions usually given for the preparation of this salt do not give a pure product; but a perfectly stable salt may be obtained by boiling together equal weights of tartaric acid, water, and iron wire for some time, and thoroughly washing the resulting sandy powder with boiling water. The salt thus obtained is a white micro-crystalline powder, nearly insoluble in water even when boiling and saturated with sal-ammoniac, or strongly acidulated with tartaric, citric, or acetic acid; easily soluble in dilute mineral acids. The solutions are optically dextrogyrate.

Ammonio-ferrie Tartrate is obtained by dissolving the ferrous salt in ammonia, whereby a thickish green solution is formed, which absorbs oxygen, becoming continually darker in colour and more viscid, but finally mobile and yellowish-red, and when exposed in thin layers to the air, dries up to garnet-red transparent laminae, easily soluble in water, insoluble in alcohol and ether. The salt when dried at 100° has the composition $C^4H^{10}Fe^2N^2O^{13} = C^4H^7(NH^4)(Fe^2)(OH)^2O^{12}$; when dried over sulphuric acid it contains in addition $3H^2O$. Its solution does not exhibit any colour-reactions with potassium ferrocyanide or thiocyanate, till it has been mixed with a mineral acid (Méhu, *loc. cit.*)

Telluric Tartrate, $Te(C^4H^4O^6)_2 \cdot 2C^4H^4O^6$. See TELLURIUM (p. 190).

Racemic Acid, $C^4H^4O^6$. According to Jungfleisch (*Compt. rend.* lxxxv. 805), the racemic acid which is formed in the manufacture of tartaric acid, owes its origin, not to the grapes, but to the action of alumina, ferric oxide, and other sesquioxides present in the liquors on the tartrates, these oxides, when not saturated with sulphuric or phosphoric acid, acting on the tartaric acid at the evaporating temperature of the liquors in such a manner as to convert it partly into racemic, partly into inactive tartaric acid. Direct experiment shows that tartaric acid, heated in closed vessels at 140° with a small quantity of aluminium tartrate, yields a considerable quantity of inactive tartaric acid.

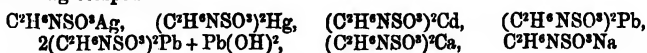
The properties of the racemic acid which Strecker obtained (vi. 1079) by the action of hydrocyanic and hydrochloric acids on glyoxal have been compared by Fr. Gail (*Ber.* xi. 1644) with those of natural racemic acid. The crystals of the synthetically prepared acid agrees with those of the natural acid in form, but do not effloresce under certain circumstances. The dehydrated synthetic acid melts at 198° (the natural at 201°). On attempting to resolve the synthetical racemic acid, through the medium of its sodio-ammonium salt, into dextro- and lævo-tartaric acid, the solution at first deposited exclusively large monoclinic crystals, destitute of hemihedral faces, and yielding an inactive solution; and it was only from the mother-liquor of these that rhombic crystals of the two acids were obtained, containing $4H^2O$, and exhibiting hemihedral faces. Precisely the same phenomena were exhibited by ordinary racemic acid.

TARTRONIC ACID, $C^3H^4O^5 = COOH.CHOH.COOH$. • *Hydroxymalonic acid.* This acid is formed by treating dihydroxymalonic acid, $C^3H^4O^6$, with sodium-amalgam; also by the action of silver bromide on monobromomalonic acid, $CO^2H.CHBr.CO^2H$ (Petrieff, *Ber.* xi. 414). Demole (*ibid.* x. 1778) prepares it by gradually adding 20 g. dinitrotartaric acid to 60 c.c. alcohol of sp. gr. 0.925 in a porcelain basin heated over a water-bath. When the evolution of gas ceases, the liquid is left to cool, and the crystals which separate are pressed between bibulous paper. They are then dissolved in water; the solution is evaporated to dryness; and the residue is treated with ether to remove oxalic acid. The tartronic acid thus prepared melted at 150° – 151° , whereas that which Grimaux obtained (*Ber.* x. 903) by the action of baryta-water on dibromopyruvic acid is described by him as melting at 145° – 147° .

TAURINE, $C^2H^7NSO^3$. Strecker, by the action of heat on ammonium isethionate, obtained a body of this composition which he regarded as taurine (v. 699). This body has also been prepared and further examined by H. Seyberth (*Ber.* vii. 391). When ammonium isethionate, melting at 135° (Strecker gives 130° as the melting point), was heated for several days in an oil-bath at 210° – 230° , it remained quite unaltered; but on heating the mass to 230° – 240° decomposition set in. The viscid syrup obtained after about eight hours' heating was dissolved in water; the solution boiled with animal charcoal and evaporated; the residue crystallised from alcohol; and the nodules which separated were boiled with alcohol, in which they were nearly insoluble, till they melted constantly at 190° – 193° . The body thus obtained gave off ammonia when boiled with potash, dissolved very easily in water, appearing indeed to be hygroscopic, and had the composition of taurine. Since, however, taurine does not melt, even at 240° , and reacts differently with potash-ley, the compound obtained as above must be regarded, not as identical with it, but as the true amide of isethionic acid.

Taurine is but slowly attacked by potassium permanganate, its sulphur being only incompletely oxidised (Guarreschi, *Ber.* xi. 1383).

Metallic Derivatives of Taurine.—J. Lang (*Bull. Soc. Chim.* [2], xxv. 180), by treating solutions of taurine with the oxides or hydroxides of various metals, has obtained the following compounds:



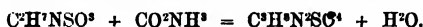
A very stable mercury-compound, $(C^2H^4NSO^3)^2Hg.HgO$, is described by R. Engel (*Bull. Soc. Chim.* [2], xxiii. 532).

Methyltaurine, $C^2H^4NSO^3 = C^2H^4(NH.CH^3)SO^3H$ (E. Dittreich, *J. pr. Chem.* [2], xviii. 592). This compound is formed by heating silver chlorethyl-sulphate (10 pts.) with solution of methylamine (30 pts. saturated at 0°) or methylamine chlorethyl-sulphate (20 pts.) with methylamine solution (30 pts.) for five or six hours at 110° – 120° , the latter process giving the best yield. In either case the liquid is boiled with caustic baryta till the odour of methylamine is no longer perceptible, then freed from baryta, and evaporated to dryness; and the residue is several times exhausted with alcohol, and repeatedly crystallised from water.

Methyltaurine, thus obtained, crystallises in long triclinic prisms having a vitreous lustre, melting at 241° – 242° , nearly insoluble in alcohol and ether, easily soluble in water (7.5 times more readily than taurine), the solution having an acid reaction. It also dissolves in strong acids and in alkalis, but without combining with them, and is separated from the alkaline solutions by alcohol. It is decomposed by melting alkalis with separation of methylamine, and converted by nitrous acid into isethionic acid.

TAUROCARBAMIC ACID, or *Uramido-isethionio acid*, $C^2H^3N^2SO^4 = CH^2.NH.CO.NH^2$
 (E. Salkowski, *Ber.* vi. 744, 1191). This acid may be formed syn-

thetically by a process analogous to that by which Wislicenus obtained hydan-toic acid (p. 1044). The mixed aqueous solution of taurine and potassium cyanate in molecular proportions is evaporated to a syrup, whereby on cooling a solid crystal-line mass is obtained, consisting chiefly of potassium taurocarbamate, the aqueous solution of which, when shaken with absolute alcohol, becomes turbid and is converted in the course of a few minutes into a pulp of needle-shaped crystals. On mixing the aqueous solution of this potassium salt with an equivalent quantity of sulphuric acid and with alcohol, and leaving the alcoholic extract to evaporate, the free acid crystal-lises out, and may be freed from adhering potassium sulphate and accidental traces of taurine by recrystallisation from dilute alcohol. The yield is very nearly equal to the theoretical quantity. Taurocarbamic acid is also formed from taurine in the animal organism by addition of carbamic acid and elimination of water:



It passes out in the urine in the form of a salt, and may be obtained therefrom by exactly precipitating the liquid with basic lead acetate, filtering after twenty-four hours, removing the lead by hydrogen sulphide and evaporating, these processes being repeated several times if necessary. The strongly concentrated liquid is then pre-cipitated with absolute alcohol, the precipitate dissolved in water, and decolorised with animal charcoal; and the precipitation with alcohol is several times repeated. The crude sodium salt thus obtained is mixed with sulphuric acid and alcohol, and on leaving the liquid to evaporate, at a rather low temperature, free taurocarbamic acid is obtained in the form of a strongly acid syrup. It may be freed from excess of sulphuric acid by baryta, from hydrochloric acid by silver carbonate, and from excess of silver by hydrogen sulphide, and separates gradually from the concen-trated filtrate in granular masses, which may be purified by pressure and recrystal-lisation.

Taurocarbamic acid crystallises in shining, quadratic, anhydrous laminæ, somewhat hygroscopic in moist air, easily soluble in water, sparingly in alcohol, insoluble in ether. The *barium salt* separates from hot alcohol in small, anhydrous, highly lustrous, rhombic, tabular crystals grouped in druses. The *silver salt* forms long radiating tufts of crystals.

Taurocarbamic acid heated for several hours at 130° – 140° with saturated *baryta-water*, is completely resolved into carbon dioxide, ammonia, and taurine, according to the equation:



without separation of even a trace of sulphuric acid.

TAUROCYNAMINE, $C^2H^3N^3SO^3$, is formed by heating equivalent quantities of taurine and cyanamide with a quantity of water sufficient to dissolve them, for four or five hours at 110° – 112° , or by leaving the mixed solution to itself for some time, and separates in small white prisms melting at 224° – 226° , easily soluble in water, in-soluble in alcohol and ether; it dissolves in strong acids, but does not combine with them (E. Dittreich, *J. pr. Chem.* [2], xviii. 63).

Methyltaurocynamine, $C^2H^3N^3SO^3 = C^2H^3NSO^3 + CN^2H^2$, formed in like man-ner from cyanamide and methyltaurine, crystallises in large prisms which have a vitreous lustre, give off their water at 110° , are insoluble in alcohol and ether, and only slightly soluble in cold water. It dissolves in strong acids, but does not form salts (Dittreich).

TEA. The composition of several kinds of tea has been examined by R. Weyrich (*Russ. Zeitschr. Pharm.* 1873, 322 and 353) with the following results. The cheaper sorts of yellow and green tea are richer in theine than the better sorts, but in black tea the contrary holds good. The differences in the total amount of ash, and in the portion soluble in water in the several kinds of tea are very small, and exhibit such irregularities that it is impossible to estimate the value of a tea by the amount of ash

contained in it. The same remark applies to the amount of potash. The proportion of phosphoric acid increases in general with the goodness of the tea, and may therefore be taken as a measure of its value. The estimations of the portion of tea which is soluble in water, and the determinations of nitrogen, showed great irregularities. Hence Weyrich considers, contrary to the view expressed by Zöller (vii. 1148), that the comparative value of unadulterated teas cannot be determined by chemical analysis.

Two samples of tea from Cachar: (1). from *Thea viridis*; (2), from a hybrid variety, have been analysed by Hodges (*Chem. News*, xxx. 114):

100 pts. of each gave the following results:

	(1).	(2).
Moisture	16.06	16.20
Organic matters	78.81	78.98
Mineral matters	5.13	4.82

The ash of each respectively consisted of—

Potash	35.200	37.010
Soda	4.328	14.435
Chlorine	3.513	2.620
Sulphuric acid	5.040	6.322
Phosphoric acid	18.030	9.180
Iron oxide	2.493	2.463
Manganous oxide	1.024	0.800
Lime	8.986	5.533
Magnesia	4.396	5.910
Sand and silica	0.500	1.300
Charcoal	2.900	1.830
Carbonic acid	13.590	12.600
	100.000	100.003

A. Winter Blyth (*Chem. News*, xxx. 212) found in genuine black tea from India:

Extractive	33.900 per cent.
Soluble ash	2.863
Insoluble ash	3.288
Tannin	11.500
Total ammonia	0.850

In a sample of Chinese tea which contained no theine, H. Weippen (*Arch. Pharm.* [3], v. 9) found cinnamic acid, probably derived from storax, which had been added to the tea for the sake of its odour.

An elaborate examination of Chinese tea has been made by Eder (*Dingl. pol. J.* cccxxi. 445, 526; *Chem. Soc. J.* xxxvi. 851-856).

Theine.—The quantity of this alkaloïd in tea is determined by Markownikoff (*Ber.* ix. 1312) as follows. 15 g. pulverised tea are drenched with 500 c.c. water and boiled, with addition of 15 g. calcined magnesia to every 5 g. tea. The precipitate is filtered off and washed, the filtrate evaporated to dryness with addition of a small quantity of magnesia; the theine extracted from the residue with benzene; the solvent evaporated; and the theine weighed.

The following quantities of theine have been found by Petrik (*Dingl. pol. J.* ccxviii. 220) in various kinds of tea.

Kaisow Congo	2.4 per cent. theine
" "	1.7 " "
" "	1.5 " "
Finest Gunpowder	1.4 " "
" Mayune Gunpowder	2.1 " "
" Souchong	2.12 " "
Tea-dust (10.8 per cent. ash)	1.46 " "

Tannin.—According to J. T. Clark (*Amer. Chem.* vii. 44), the proportion of tannin in tea varies from 5 to 19 per cent.

Paraguay tea from *Ilex paraguayensis* is, according to Byasson (p. 1496), destitute of tannin; according to Robins, on the contrary (*Pharm. J. Trans.* [3], viii. 1027), it contains, as an average of seven samples, 10 to 16 per cent. of that substance.

Mineral Constituents of Tea.—G. Wigner (*Pharm. J. Trans.* [3], iv. 909; vi. 261, 281, 402; *Chem. News*, xxxii. 166, 180, 235) has determined in several sorts of tea

the total amount of ash, the quantities soluble in water and in hydrochloric acid, and the amount of alkali reckoned as potash. The following are the results:

	Total ash	Ash soluble in water	Ash soluble in HCl	Silica	Alkali reckoned as potash
Mean of 24 sorts ⁽¹⁾	5.66	3.01	2.21	0.44	1.62 p. c.
" 17 " ⁽²⁾	5.75	3.07	2.25	0.43	1.38 "
" 18 " ⁽³⁾	5.80	3.44	2.04	0.32	1.39 "
" 4 " ⁽⁴⁾	5.57	2.92	2.10	0.55	1.59 "
" 12 " ⁽⁵⁾	5.77	2.99	2.22	0.56	1.67 "
" 9 " ⁽⁶⁾	6.25	3.07	2.19	0.99	1.35 "

(¹) Taken from original chests. (²) Ordinary sorts from original chests. (³) Fine sorts from original chests. (⁴) Especially fine sorts. (⁵) From retail dealers. (⁶) Gennino Capers.

Similar determinations of the ash of ten sorts of tea have been made by A. I. Wilson (*Chem. News*, xxviii. 307):

	Total ash	Ash soluble in water	Ash soluble in HCl	Silicates	Ferric oxide
Moning . . .	6.00	3.15	2.03	0.82	0.05
" . . .	5.82	2.73	2.52	0.57	0.07
" . . .	5.90	2.76	2.36	0.78	0.07
" . . .	5.55	2.66	2.21	0.68	0.09
Kaisow . . .	5.43	3.33	1.88	0.22	0.05
Feechow Pekoe . . .	6.15	3.20	2.16	0.79	0.09
Assam Souchong . . .	5.15	2.90	2.05	0.20	0.03
Green Assam . . .	5.32	2.94	2.11	0.27	0.08
Fine green tea . . .	7.14	2.38	3.19	1.57	0.12
Mixed black tea . . .	5.68	2.86	2.33	0.49	0.04

Six kinds of tea examined by Wanklyn (*Chem. News*, xxviii. 186) gave, on the average, a quantity of ash equal to 5.92 per cent. of the dried tea, of which 3.55 pts. were soluble in water and 2.37 insoluble. As tea which has been exhausted with water contains a smaller proportion of soluble ash-constituents than fresh tea, Wanklyn recommends the determination of the total ash and of the amount of soluble constituents as a means of judging of the value of the tea.

The ash of black and of green tea was found by Wigner to contain:

	K ² O	Na ² O	SO ³	CO ²	SiO ²
Black	30.92	1.68	4.88	11.60	1.70
Green	28.42	2.08	5.66	6.43	7.50

The proportion of constituents soluble in water was in the black tea, 57.00 per cent.; in the green 52.85.

On the Detection of Adulterations in Tea, see A. H. Allen (*Chem. News*, xxviii. 210, 275, 303; xxix. 129, 140, 157, 189, 221; xxx. 2; *Chem. Soc. J.* xxvii. 191; xxviii. 786; *Jahresb. f. Chem.* 1873, 973; 1874, 1040).

On the Agricultural Chemistry of the Indian Tea-plantations, see J. Campbell-Brown (*Chem. Soc. J.* [1875], xxviii. 1217-1228).

TEAK-WOOD. A white deposit in the wood of this tree (*Tectonia grandis*) has been analysed by G. Thoms (*Landw. Versuchs.-St.* xxii. 68, xxiii. 413), and found to consist of monocalcic orthophosphate, CaHPO⁴. The formation of this deposit leads to the idea that the wood itself must contain a considerable quantity of phosphoric acid, and analysis shows that this is really the case, the composition of the ash of the wood being as follows:

CaO	MgO	FeO	K ² O	Na ² O	SiO ²	SO ³	P ² O ⁵	CO ²	Cl
31.35	9.74	0.80	1.47	0.04	24.98	2.22	29.69	0.01	0.01 = 100.31

The percentages of carbon and hydrogen are higher than in most woods, and this, together with the richness in calcium phosphate and silica, may perhaps account for the great hardness of the wood,

TELLURIUM. *Preparation.*—1. H. Schnitzler (*Dingl. pol. J.* cxi. 484 and 492).

Tellurium-potassium Bromide, $\text{TeBr}_4 \cdot 2\text{KBr}$.—To prepare this salt, equivalent quantities of potassium bromide and tellurium are placed in a flask, and water is added till the potassium bromide dissolves; bromine is then run in, and the flask shaken till the tellurium disappears; and the resulting orange-yellow liquid, filtered from a small yellow deposit, is evaporated over the water-bath, the double salt then separating in crystals which may be purified by recrystallisation (Wills, *loc. cit.*) These crystals, according to H. Baker, are orthorhombic. $a : b : c = 1.0000 : 1.4901 : 1.3658$.

Observed forms, P, 0P, $\infty P\infty$. Type pyramidal, or $+\frac{P}{2}$, $-\frac{P}{2}$. Faces P perfectly smooth, and with a brilliant lustre; those of 0P and $\infty P\infty$ are uneven. At 120° the salt loses water and becomes orange-coloured, but remains quite constant in weight between 120° and 160°.

Oxides and Acids. The specific gravities of the following compounds have been determined by F. W. Clark (*Sill. Am. J.* [3], xiv. 281; xvi. 401):

Tellurous oxide, TeO^2	5.7559 at 12.5° and 5.7841 at 14°
Telluric oxide, TeO^3	5.0704 „ 14.5° „ 5.0794 „ 10.5°
„ „ another specimen	5.1118 „ 11°
Telluric acid, H^2TeO^4	3.425 „ 18.8° „ 3.458 „ 19.3°
	3.410 „ 19.2°
„ „ (cryst.) $\text{H}^2\text{TeO}^4, 2\text{H}^2\text{O}$	2.999 „ 25.5° „ 2.9649 „ 26.5°
Ammonium tellurate, $(\text{NH}^4)^2\text{TeO}^4$	3.024 „ 24.5° „ 3.012 „ 25°

Barium Tellurate slightly heated gave 4.5486 at 10.5°, and 4.5305 at 10°; another specimen gave 4.4811 at 16°. The sp. gr. of the salt merely dried at 200° was nearly 4.2.

Thallium Tellurate, precipitated by mixing the solutions of ammonium tellurate and thallium nitrate, and dried at 100°, had a sp. gr. of 5.687 at 22°, and 5.712 at 20°; after heating to about 180°, with loss of 1.46 per cent. water, its sp. gr. was 6.742 at 16°, and 6.760 at 17.5°.

Tellurous Oxide is formed, with evolution of sulphurous oxide, when tellurium is heated in sulphuric acid, and if considerable quantities are operated on, separates on cooling in the crystalline form (A. Hilger, *Liebig's Annalen*, clxxi. 211).

Tellurous Acid, like selenious acid, is completely precipitated by a magnesium salt and ammonia, but the precipitate is amorphous, whereas that obtained with selenious acid is crystalline (Hilger a. von Gerichten, *Zeitschr. anal. Chem.* 1874, 132).

Telluric Acid, H^2TeO^4 , is best prepared by boiling a solution of tellurous acid in nitric acid with lead dioxide, precipitating the lead from the filtrate by sulphuric acid, evaporating on the water-bath, digesting the residue with alcohol and ether to remove excess of sulphuric acid, dissolving the residue then left in a small quantity of hot water, and recrystallising it in a vacuum (F. Becker, *Liebig's Annalen*, clxxx. 257).

On the reduction of Telluric Acid by *Grape-sugar*, see p. 1895.

A mercurous tellurate, Hg^2TeO^4 , called *Magnolite*, and a ferrous tellurate, FeTeO^4 , called *Ferrotellurate*, are described by F. A. Genth (*Zeitschr. Kryst.* ii. 7). Both occur in the upper veins of the Keystone Mine, Magnolia District, Colorado, the former in microcrystalline groups sometimes enclosing quicksilver, associated with brown hematite, psilomelane, and quartz as a product of decomposition of coloradoite; the latter containing a small quantity of nickel, and occurring as a crystalline coating on quartz.

Sulphides. The statement of Berzelius that hydrogen sulphide throws down TeS^2 from a solution of tellurous acid, and TeS^3 from telluric acid, requires, according to Becker (*Liebig's Annalen*, clxxx. 257), a certain amount of correction, his observations showing that the precipitates thus obtained give up nearly all their sulphur when treated with carbon sulphide, and consequently are not definite chemical compounds, but merely mixtures of tellurium and sulphur in approximately constant proportions. He, however, thinks it probable that sulphides of tellurium are formed in the first instance, since, on closely observing the change which takes place when hydrogen sulphide is passed into tellurous acid, each bubble of the gas is seen to produce a red precipitate which turns black only when it reaches the surface of the liquid.

Tellurium Minerals. 1. *Native Tellurium*.—Four varieties of native tellurium from Colorado have been analysed by F. A. Genth:

1. In crystals often enclosing quartz, or in plates between masses of ore consisting of calaverite, coloradoite, iron pyrites, and a mineral perhaps allied to roscelite; sp. gr. = 6.275; from the Keystone Mountain, Lion, and Dunraven Mines, Magnolia District, Boulder County. 2. Tumefied mass looking as if it had been fused, and evidently consisting—in spite of apparent homogeneity—of a very intimate mixture of tellurium with quartz and silicates. Sp. gr. = 4.005; from the Mountain and Lion Mines; called by the finder *Lionite*. 3. Very small, shining, much distorted crystals in cavities of quartz: from Smuggler's Mine, Ballarat District, Boulder County. 4. Sample of tellurium occurring in very large masses (up to 12 kilo. in weight):

granular to cauliform) in cavities, and oxidised on the surface to tellurous oxide: in the John-Jay Mine, Central District, Boulder County, at a depth of 9-10 meters.

	Te	Au	Ag	Hg	Cu	Pb	Fe	V ² O ³	X (%)	
1.	96.91	0.60	0.07	trace	—	—	0.78 (2)	0.49	1.15 (3)	= 100 (4)
2a.	55.86	1.38	0.25	—	—	—	—	—	41.52 (5)	= 99.01
b.	55.54	1.53	0.25	—	—	—	—	—	42.50 (6)	= 99.82
3a.	92.29	3.40	1.69	1.07	0.51	0.74	0.12	—	0.12 (7)	= 99.94 (8)
b.	93.64 (9)	2.18	1.15	1.34	0.43	1.02	0.18	—	0.06	= 100 (10)
4.	97.94	1.04	0.20	—	—	—	0.89	—	—	= 100.07 (11)

(1) Various. (2) FeO. (3) Al₂O₃, MgO, K₂O. (4) After deduction of 8.90 per cent. quartz. (5) Consisting of 34.72 per cent. SiO₂, 6.15 Al₂O₃ and Fe₂O₃, 0.17 MgO, 0.48 CaO. (6) Consisting of 35.91 per cent. SiO₂, 6.14 Al₂O₃ and Fe₂O₃, 0.19 MgO, 0.26 CaO. (7) MgO. (8) After deduction of 28.04 per cent. quartz. (9) Estimated by difference. (10) After deduction of 65.24 per cent. quartz. (11) After deduction of 14.08 per cent. quartz, including, however, 0.32 per cent. zinc.

2. *Metallic Tellurides*.—The following tellurides from California are described by H. J. Burkart (*Jahrb. f. Min.* 1873, 476) and by F. A. Genth (*J. pr. Chem.* 1874, [2], x. 355).

Bismuth Telluride, or *Tetradymite*, Bi²Te³.—The variety of this mineral which contains sulphur (v. 707) has been found in small quantities in some new localities, the most interesting of which is Uncle Sam's Mine, Highland District, Montana, where it is accompanied by gold and quartz; it is also found in dolomite. It is partly converted by oxidation into montanite (bismuth tellurate), and consequently evolves chlorine when heated with hydrochloric acid, the telluric acid contained in it being at the same time reduced to tellurous acid. Tetradymite occurs both in laminæ, up to $\frac{3}{4}$ inch broad, and in scales. Colour blue-grey and iron-black, frequently variegated. *Analyses*: (1). Broad laminæ. (2). Small scales from the dolomite:

Te	Bi	Au	Cu	Fe	Se	S	Quartz	Sp. gr.
34.90	60.49	0.21	trace	0.09	trace	4.26	0.05 = 100.00	7.332
34.41	59.24	—	0.47	—	0.14	5.16	0.58 = 100.00	7.542

It is remarkable that the tetradymite from Uncle Sam's Mine contains sulphur, while that from the gold-washings of Highland does not.

Montanite or *Bismuth Tellurate*, Bi₂O₃.TeO₃ + H₂O (or 2H₂O).—This mineral, formed by oxidation of tetradymite, was first observed by Genth during the examination of the tetradymite of Highland in Montana; subsequently the so-called tetradymite from Davidson Co., North Carolina, which was in great part oxidised, and gave off chlorine when treated with hydrochloric acid, was found to be identical with it. The 'yellow bismuth oxide' from Whitehall in Virginia, analysed by Jackson (*Am. J. of Sci.* [2], x. 78), is also regarded by Genth as probably the same mineral.

Montanite is not crystallised, but exhibits here and there the scaly structure of the original tetradymite, and is in reality a pseudomorph after the latter, on which it forms a coating. It is earthy, soft, dull to waxy in lustre, yellowish to white, and opaque. Before the blowpipe it exhibits the reactions of bismuth and of tellurium, and gives off water when heated in a tube.

Genth's analyses lead to the following results:

	I	Oxygen	II	Oxygen	III	Oxygen
Ferric oxide . . .	0.56	—	1.26	—	0.32	—
Lead oxide . . .	0.39	—	—	—	—	—
Cupric oxide . . .	—	—	1.04	—	1.08	—
Bismuth oxide . . .	66.78	6.85	68.78	6.29	71.90	7.37
Tellurous oxide . . .	26.83	7.30	25.45	7.05	23.90	6.51
Water . . .	5.74	—	3.47	—	2.86	—
	100.30		100.00		100.06	

The oxygen ratio between the bismuth oxide and the tellurous oxide is nearly 1:1, but it is as yet uncertain whether the composition of the mineral is Bi₂O₃.TeO₃.H₂O or Bi₂O₃.TeO₃.2H₂O.

Lead Telluride or *Altaite*, PbTe, occurs at Red Cloud Mine, and at King's Mountain, Gaston Co. N.C.: at the latter locality in fine-grained quartz, accompanied by gold, galena, copper pyrites, fahl-ore, iron pyrites, and a greenish micaceous mineral resembling fuchsite, and rarely with nagyagite. One very small cubical piece was obtained which consisted partly of galena and partly of altaite, as was evident by the colours of the two, though there was no break in the surface of the specimen. At Red Cloud the altaite is found in larger quantities, together with native tellurium, sylvanite, pyrites, siderite, and quartz. It is sometimes found in small imperfect

cubes, usually coated with galena; more rarely in large cleavable masses: most frequently in coarse grains, which sometimes show an imperfect cubical cleavage, and a fracture inclining to conchoidal. It is distinguished from other tellurium ores by its tin-white colour, inclining to greenish-yellow. It contains:

SiO ²	Au	Ag	Cu	Pb	Zn	Fe	Te
0.19	0.19	0.62	0.06	60.22	0.15	0.48	37.99 = 99.90
0.32	0.16	0.79	0.06	60.53	0.04	0.33	37.51 = 99.74

Altaite occurs also, mixed with hessite and petzite, in the Stanislaus and Golden Rule Mines, California. Two specimens gave: (1) after deduction of 1.03 per cent.; (2) after deduction of 1.96 per cent. quartz:

	Pb	Ag	Au	Te
(1).	60.71	1.17	0.26	37.31 = 99.45
(2).	47.84	11.30	3.86	37.00 = 100

These numbers show that (1) consisted of 99.25 per cent. altaite and 2.20 hessite; (2) of 77.42 altaite and 23.11 hessite.

Tellurides of Silver and Gold.—Hessite and Petzite. Auriferous silver tellurite or petzite is the most abundant of all the Californian tellurium ores. The specimens from the Stanislaus and Golden Rule mines are destitute of crystalline structure, exhibit a distinctly conchoidal fracture, metallic lustre, steel-grey to iron-black colour, and iron-black streak; hardness = 2.51, sp. gr. 9.94. Analyses gave 24.80–25.70 per cent. gold, 40.60–42.36 silver, and 31.64–34.16 tellurium, agreeing with the formula $\text{Au}^{27}\text{Te}_3\text{Ag}^{37}\text{Te}$. They contain, therefore, more gold than the petzite or sylvanite of Nagyag, but need not on that account be regarded as a distinct species, inasmuch as gold can replace silver in various proportions. Petzite is also found abundantly in the Red Cloud Mine at Gold Hill, Boulder Co., Colorado.

Hessite, Ag^{27}Te , containing little or no gold, is found in the Stanislaus Mine, but always mixed with other minerals, viz., native gold, altaite, and quartz. It is altogether a rare mineral. Genth obtained one specimen of a dark iron-grey colour inclining to black. It was granular, with uneven cleavage, and gave a dark lead-grey powder; soft; sp. gr. 8.178. It contained cavities lined with small crystals of heavy spar and pyrites. The differences in external characters between the other varieties of hessite are very small; those rich in gold are brighter and more brittle.

Analyses: 1 and 2. The pure hessite just described; 3, 4, and 5. Auriferous hessite containing from 3.3–13 per cent. gold; 6 and 7. Petzite containing more than 24 per cent. gold:

	Te	Au	Ag	Cu	Pb	Fe	Zn	Bi	Quartz	Sp. gr.
(1).	37.86	0.22	59.91	0.17	0.45	1.35	trace	—	— = 99.96	8.178
(2).	38.07	0.20	60.19	0.16	0.18	1.20	trace	—	— = 100	
(3).	37.60	3.31	59.68	0.05	—	0.15	—	—	0.18 = 100.97	8.789
(4).	36.74	3.34	59.83	0.06	—	0.21	—	—	0.13 = 100.31	
(5).	34.91	13.09	50.56	0.07	0.17	0.36	0.15	—	0.70 = 100.01	8.897
(6).	33.49	24.10	40.73	trace	0.26	0.78	0.05	0.41	0.62 = 100.44	9.010
(7).	32.97	24.69	40.80	trace	—	1.28	0.21	—	0.05 = 100	9.020

For auriferous hessite and petzite the atomic relations are as follows:

	Au	Ag	Te
Auriferous hessite 3 and 4	1	32.7	34.3
" 5	1	7	8.2
Petzite 6 and 7	1	3.1	4.2

Sylvanite or Graphitic Tellurium. For this mineral the Red Cloud Mine is the first authenticated locality in the United States. It occurs sometimes massive, with very distinct cleavage, sometimes in the well-known graphic forms (v. 647), and always very intimately mixed with iron pyrites.

Analysis: 1–3 by Genth (*J. pr. Chem.* [2], x. 355); 4. Sylvanite from Grand View Mine, Colorado, where it occurs imbedded in quartz, and intimately mixed with pyrites; a. Direct result of analysis, the sulphur, however, being calculated from the amount of iron as FeS^2 ; b. After deduction of FeS^2 :

	Te	Se	S	Au	Ag	Cu	Pb	Fe	Zn	Quartz	Sp. gr.
1.	56.31	trace	1.82	24.83	13.05	0.23	—	3.28	0.45	0.32 = 100.29	7.943
2.	54.60	trace	4.44	23.06	11.52	0.57	—	4.64	0.11	0.86 = 100	
3.	58.87	trace	1.06	25.67	11.92	0.21	0.46	1.17	0.06	0.59 = 100	
4a.	52.96	—	5.62	26.89	10.35	—	—	4.45	—	— = 99.77	7.943
4b.	58.91	—	—	29.35	11.74	—	—	—	—	— = 100	

Genth's analyses lead to the following atomic proportions :

	Au :	Ag :	Te :	(Au,Ag) :	Te
1. . . .	1 :	0.96 :	6.98 . .	1 :	3.6
2. . . .	1 :	0.91 :	7.29 . .	1 :	3.8
3. . . .	1 :	0.84 :	6.45 . .	1 :	3.5

Calaverite. This mineral, from the Keystone and Red Cloud Mines, has again been analysed by Genth (*Zeitschr. f. Kryst.* ii. 6), with results agreeing nearly with those of his former determinations (p. 371), and leading to the formula $(AuAg)Te^2$. The material obtained from the Keystone and Mount Lion Mines formed indistinct and unmeasurable crystals belonging either to the rhombic or to the monoclinic system, indistinctly cleavable, and having, after deduction of quartz, with which it was interpenetrated, a density of 9.043. Composition :

	Au	Ag	Te	V ² O ⁵	FeO	X (%)
1 (found).	38.75	3.03	57.32	0.05	0.30	0.55 = 100
2 (found).	38.91	3.08		not determined		—
3 (calc.)	39.01	3.06	57.93			= 100

* Al²O³, MgO, &c.

Krennerite. A tellurium mineral from Nagyag in Transylvania, described by J. A. Krenner (*Ann. Phys. Chem.* [2], i. 636), who regards it as chemically and crystallographically distinct from sylvanite. It has not been analysed quantitatively; qualitative analysis detected nothing but tellurium and gold. It occurs implanted on quartz in small light steel-grey crystals, generally much weathered. The crystals are rhombic, and cleave parallel to the basal face. Observed faces, $\infty P \infty$, $\infty P \infty$, OP , ∞P , ∞P_2 , ∞P_3 , ∞P_3 , ∞P_2 , $P \infty$, P_2 . Fundamental angles, $\infty P : \infty P = 86^\circ 20'$; $\infty P : P \infty = 71^\circ 53'$. From sylvanite, which Krenner also regards as rhombic, it differs by values amounting to 1° in the inclination of the corresponding faces. (†, vom Rath (*Berl. Acad. Ber.* 1877, 292) observed the faces P , P_2 , $\frac{2}{3}P_3$, $P \infty$, $P \infty$, $\frac{1}{2}P \infty$, ∞P , ∞P_2 , ∞P_3 , $\infty P \infty$, OP . He also found the angle $\infty P : \infty P$ to have the value $86^\circ 30'$, nearly the same as that found by Krenner, whence he calculates the axial ratio $a : b : c = 0.940706 : 1 : 0.504455$. According to Schrauf (*Zeitschr. Kryst.* ii. 209), this ratio is 0.93961 : 1 : 0.50733.

Coloradoite or **Mercuric Telluride**, HgTe (Genth, *Jahrb. f. Min.* 1877, 949; *Zeitschr. f. Kryst.* ii. 4). This mineral is found, together with tellurium and quartz, in the Keystone and Mount Lion Mines, and together with tellurium and gold in the Smuggler Mine, Colorado. It is massive, somewhat granular, sometimes (especially if mixed with sylvanite) indistinctly cauliform; does not exhibit either crystalline form or cleavability. It is always intimately mixed with tellurium, tellurite, gold, sylvanite, quartz, and oxidation-products; the purest specimens that could be obtained had a density of 8.627.

Analyses.—1-5. From the Keystone Mine. 6 and 7. From the Smuggler Mine, Ballarat District, at a depth of 2.5-3 meters. In these last two analyses, the gold and silver have not been deducted, since Genth regards them as essential :

	1	2	3	4	5	6	7
Quartz }	28.50 (†)	46.83 (†)	25.18 (†)	8.46 (†)	20.72 (†)	2.90 (†)	3.05 (†)
Gold }	—	—	—	—	—	3.46	7.67
Silver	—	—	—	—	—	2.42	7.18
Copper	—	—	—	—	—	trace	0.16
Zinc	—	—	—	—	—	"	0.50
Iron	—	—	—	—	—	1.35	0.92
Mercury	56.33	52.28	51.48	49.80	45.63	55.80	48.74
Tellurium	43.81	42.95	44.25	46.74	50.05	36.24	34.49
Al ² O ³ Fe ² O ³	trace	2.44	not determined		—	—	—
V ² O ⁵	"	0.70	"	"	"	—	—
MgO	"	0.11	"	"	"	—	—
CrO	"	0.84	"	"	"	—	—
K ² O	"	trace	"	"	"	—	—
Totals	100.14	99.32	—	—	—	99.27	99.66

(†) Deducted from the total.

According to these results, the samples consist of :

	1	2	3	4	5	6	7
HgTe	92.38	85.74	84.43	81.67	74.83	91.51	79.93
Te	7.76	9.49	11.30	14.87	20.85	—	—

Material from still greater depths in the Smuggler Mine was found to consist merely of native tellurium, mixed with 1.75–2.20 per cent. coloradoite.

The following crystallographic determinations of native tellurides from Transylvania have been made by A. Schrauf (*Zeitschr. f. Kryst.* ii. 209; *Jahrb. f. Min.* 1878, 862):

Sylvanite: Monoclinic; $a : b : c = 1.63394 : 1 : 1.12653$; $\beta = 90^\circ 25'$. Three types are distinguished according as the crystals cross one another at angles of $69^\circ 44'$, $55^\circ 8'$, or 90° .

Krennerite (White Tellurium, Mullerin, Yellow ore): rhombic; $a : b : c = 0.9361 : 1 : 0.50733$.

Nagyagite (telluride of lead and gold, iv. 1): rhombic, or monoclinic, with an axial angle $= 90^\circ \pm 1^\circ$, but not quadratic; $a : b : c = 0.2807 : 1 : 0.2761$.

Telluric Silver-glance (Hessite, Petzite), Ag^2Te . Monometric.

Telluric Silver-blende (Stützite): a new species, probably Ag^2Te . Monoclinic; $a : b : c = 1.73205 : 1 : 1.25829$; $\beta = 89^\circ 33'$.

Tellurium Ochre.—This mineral, hitherto found only in Transylvania (v. 713), occurs also in the Keystone, Smuggler, and John-Jay Mines, Boulder County, Colorado, in cavities or clefts of native tellurium, sometimes in single crystals, sometimes in tufted groups of crystals (probably rhombic), mostly of prismatic habit, sometimes acutely pyramidal and cleavable in one direction (Genth, *Jahrb. f. Min.* 1878, 74).

Tellurium-compounds, Organic (F. Boeker, *Liebigs Annalen*, clxxx. 262).

Tellurium Tartrate, $(\text{C}^4\text{H}^4\text{O}^4)_2\text{Te} \cdot 2\text{C}^4\text{H}^4\text{O}^4$, is formed on dissolving tellurous oxide in tartaric acid, and separates on leaving the filtered solution to evaporate, in long pointed transparent crystals, which effloresce on exposure to the air, becoming white and opaque. When dried at 100° they have the composition above given.

Triethyl-tellurium Iodide or **Iodotriethyl-tellurin**, $(\text{C}^2\text{H}^5)_3\text{TeI}$, is prepared by heating ethyl telluride, $(\text{C}^2\text{H}^5)_2\text{Te}$, (ii. 550), with a slight excess of ethyl iodide in a reflux apparatus at 50° . It dissolves easily in cold water, and crystallises therefrom by evaporation in a vacuum in light yellow monoclinic plates and prisms, easily soluble in alcohol, insoluble in ether. It melts at 90° – 92° , and resolidifies at 86° . Its aqueous solution, digested with recently precipitated silver oxide, yields an alkaline liquid, from which a platinum salt may be prepared, having the composition $[\text{Te}(\text{C}^2\text{H}^5)_3\text{Cl}]^2\text{PtCl}_4$, whence it follows that the alkaline liquid contains triethyl-tellurium hydroxide, $\text{Te}(\text{C}^2\text{H}^5)_3\text{OH}$; this compound, however, like its analogues, decomposes on evaporation at the temperature of the water-bath. The platinumochloride may be prepared by mixing crude triethyltellurium chloride in aqueous solution with platonic chloride, and separates as an orange-coloured precipitate, insoluble in alcohol and ether, slightly soluble in water.

TEPHROITE. *Manganous Silicate*, Mn^2SiO_4 (v. 254).—This mineral, originally obtained from Sparta, New Jersey, has since been found: (1). In the Mine Hill Mine, Sussex, New Jersey, interpenetrated by red zinc-ore and pale green willemite. Hardness 5.5. Sp. gr. 4.00 (Mixer, *Sill. Am. J.* [2], xlv. 230). (2). At Laangban in Sweden, together with Jacobssite (Pisani, *Compt. rend.* lxxxiv. 1511). (3). At the same locality; light red; containing a considerable quantity of magnesia:

SiO_2	MnO	ZnO	FeO	MgO	CaO	Loss by ignition
29.44	57.31	7.36	0.87	2.50	2.51	0.27 = 100.26
31.70	47.70	—	0.80	9.48	9.80	— = 99.48
33.70	51.19	—	—	12.17	0.95	0.44 = 98.45

TERACRYLIC ACID, $\text{C}^7\text{H}^{12}\text{O}_2$ (O. Krafft, *Ber.* x. 521, 1659, 1740). This acid, homologous with pyroterebic acid, is produced by the action of heat on terpenylic acid, $\text{C}^9\text{H}^{12}\text{O}_4 = \text{CO}_2 + \text{C}^7\text{H}^{12}\text{O}_2$ (p. 1907). On neutralising the distillate with an alkali, removing the undissolved portion, acidulating the clear solution with sulphuric acid, and distilling, the teracrylic acid passes over with the steam in the form of oily drops. It is a colourless liquid, boiling at 216° – 218° . The *calcium salt*, $(\text{C}^7\text{H}^{11}\text{O}_2)_2\text{Ca} + 5\text{H}_2\text{O}$, is easily soluble, and crystallises in long transparent needles which effloresce on exposure to the air. The *silver salt*, $\text{C}^7\text{H}^{11}\text{O}_2\text{Ag}$, is obtained by recrystallisation from hot water in small colourless needles.

When potassium teracrylate is heated for some time on the water-bath with strong potash-ley, the teracrylic acid is converted into an isomeric acid which smells faintly of cymene, and forms a calcium salt which crystallises in needles an inch long, and is less soluble in hot than in cold water. The corresponding silver salt has not been obtained in the crystalline state. The acid of these salts fused with potash yields two acids, one of which is formic acid.

TERBIUM. See YTTRIUM-METALS.

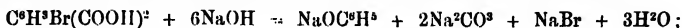
TEREBENE. See TERPENES.

TEREBIC ACID. See TERPENES.

TEREPHTHALIC ACID, or PARAPHTHALIC ACID. See PHTHALIC ACIDS (p. 1615).

Bromoterephthalic acid, $\text{C}^6\text{H}^3\text{Br}(\text{COOH})^2$, prepared by the action of potassium permanganate on bromotoluic acid, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)(\text{COOH})$, in alkaline solution, crystallises from boiling water or alcohol in microscopic needles melting at $304^\circ\text{--}305^\circ$. Contrary to the usual relations of solubility between aromatic acids and their bromine derivatives, it is more readily taken up by solvents than terephthalic acid itself. Dried at 100° it retains 1 mol. H^2O . Its *potassium salt* crystallises in silky needles; the *copper salt* is obtained as a blue crystalline precipitate; the *lead* and *silver salts* as flocculent precipitates, the last retaining 1 mol. H^2O at 100° .

Bromoterephthalic acid is decomposed by prolonged fusion with sodium hydroxide, yielding sodium phenate, carbonate, and bromide, according to the equation:



but, on adding the brominated acid to the soda in a state of fusion, stirring for a short time, and then leaving the liquid to cool, a different action takes place, resulting in the formation of hydroxyterephthalic acid:



The hydroxy-acid thus produced separates from its hot aqueous solution as a white crystalline powder, which does not melt at 330° , and is identical with the hydroxyterephthalic acid already described (p. 1534).

Bromoterephthalic Chloride, $\text{C}^6\text{H}^3\text{Br}(\text{COCl})^2$, is a colourless oily liquid, boiling at 305° . The corresponding *amide*, $\text{C}^6\text{H}^3\text{Br}(\text{CONH}^2)^2$, crystallises in colourless needles which melt at 270° , and are not dissolved at ordinary temperatures by water, alcohol, or ether.

Methyl Bromoterephthalate, $\text{C}^6\text{H}^3\text{Br}(\text{COOCH}^3)^2$, formed by treating the chloride with methyl alcohol, crystallises in needles, melts at 42° , and boils at a temperature above 300° (H. Fischli, *Ber.* xii. 615).

TERPENES, $\text{C}^{10}\text{H}^{16}$. An examination by W. A. Tilden (*Pharm. J. Trans.* [3], viii. 188) of the terpenes from the volatile oils of turpentine, juniper, savine, sage, lavender, orange, bergamot, and lemon, has led to the following conclusions. The terpenes, $\text{C}^{10}\text{H}^{16}$, so widely diffused among volatile oils, have but little influence in determining their characteristic odours. Natural terpenes are colourless, of sp. gr. $0.84\text{--}0.86$, and may be divided into two groups: 1. *Turpentine-group*. Boiling point $156^\circ\text{--}160^\circ$. Melting point of the nitroso-derivative produced by the action of NOCl , 129° . The members of this group yield solid terpin-hydrates, having the composition $\text{C}^{10}\text{H}^{16}\text{O}^2 \cdot \text{H}^2\text{O}$. 2. *Orange-oil group*. B. p. $174^\circ\text{--}176^\circ$. M. p. of nitroso-derivative, 71° . The members of this group do not yield solid terpin-hydrates. The individual members of each group are allotropic modifications of the same hydrocarbon, distinguished from one another by their specific rotatory power.

(1). *Terebenthene* and *Isoterebenthene* (J. Riban, *Compt. rend.* lxxviii. 288; lxxix. 223, 314). Terebenthene is the chief constituent of French turpentine oil, from *Pinus maritima* (v. 920), and is obtained in the pure state by washing the turpentine-oil with an alkaline ley and submitting it to fractional distillation. *Isoterebenthene* is obtained by heating terebenthene to 300° , and purified by fractional distillation and repeated rectification over sodium. It is a laevogyrate liquid, having an orange-like odour, and boiling at $173^\circ\text{--}177^\circ$ (corr.) When exposed to the air it quickly absorbs oxygen, and becomes resinous. In an atmosphere of carbon dioxide it remains unaltered, but absorbs the gas in considerable quantity. Its *hydrochloride*, $\text{C}^{10}\text{H}^{16}\text{HCl}$, is a colourless mobile liquid having a sweetish and not camphorous odour. Under ordinary pressure it boils with partial decomposition at 210° , giving off hydrogen chloride. Under a pressure of 20 mm. it boils almost without decomposition, at 110° . It does not yield any solid product either by cooling, or by spontaneous evaporation, or by distillation in a vacuum, or by treatment with fuming nitric acid. It is easily saponified by boiling with water. It is not acted upon by alcoholic potash. The *dihydrochloride*, $\text{C}^{10}\text{H}^{16}2\text{HCl}$, obtained by passing hydrogen chloride into an ethereal solution of isoterebenthene or of the monohydrochloride, forms white crystalline laminae; melts at 49.5° ; is converted into terpinol, $\text{C}^{10}\text{H}^{16}2\text{H}^2\text{O}$, by boiling with aqueous alcohol containing a small quantity of hydrochloric acid; remains unaltered when boiled with aqueous potash. It forms liquid compounds with the monohydrochloride of turpentine-oil, the isomeric solid mono-

hydrochlorides of active and inactive camphene, and the hydrochloric ether of borneol. *Isoterebenthene dibromide* is converted by boiling with potash-ley into cymene.

The following determinations of the physical properties of terebenthene and isoterebenthene have been made by Riban (*Compt. rend.* lxxviii. 788; lxxix. 314). Terebenthene boils at 156.5° (corr.); isoterebenthene at 175° . The optical rotatory power of terebenthene is $\alpha_D = -40.32^{\circ}$; that of isoterebenthene $\alpha_D = -9.44^{\circ}$ at 23° .

Specific Gravity.

Temp.	Terebenthene	Temp.	Isoterebenthene
0°	0.8767	0°	0.8586
17.88	0.8619	20.28	0.8427
39.74	0.8439	40.19	0.8273
59.38	0.8277	58.32	0.8131
79.59	0.8107	79.24	0.7964
		100.00	0.7793

Indices of Refraction.

Spectral lines	Wave-lengths acc. to Thalen	Terebenthene at 16°	Isoterebenthene at 25°
Red (Hydrogen)	0.00065618	1.4665	1.4677
Yellow (Sodium)	0.00058920	1.4697	1.4709
Green (Magnesium)	0.00051739	1.4740	1.4760
Blue (Magnesium)	0.00044810	1.4808	1.4839

The refractive index of terebenthene for the line D at 25° is 1.4648.

On Tetraterebenthene see p. 1917.

(2). Tilden (*Chem. Soc. J.* [1878], xxxiii. 80) has examined the terpenes from Russian turpentine-oil (from *Pinus sylvestris* and *P. Ledebauri*), and from the needles of *P. sylvestris*. The former, when freed from small quantities of creasote and acetic acid by agitation with soda-ley, yielded by distillation a terpene which boiled at 157° , and with the exception of its rotatory power ($+23.3^{\circ}$) agreed in its properties with australene (v. 921). The same oil further contained a considerable quantity of a second hydrocarbon, $C^{10}H^{16}$, boiling between 171° and 171.5° , having a density of 0.86529 at 15° , and a specific rotatory power of $+17^{\circ}$, and finally cymene. The oil from the needles of *Pinus sylvestris* contained, in addition to a hydrocarbon identical with australene (rot. power $+18^{\circ} 48'$), a terpene, agreeing with that above mentioned in boiling-point (171°) and density, but lævogyrate (about -4°), together with a small quantity of cymene.

(3). Flawitzky (*Ber.* xi. 1846), by distilling Russian turpentine-oil with steam and rectifying the product, has obtained a dextrogyrate terpene having a greater rotatory power than that described by Tilden; $[\alpha]_D = 27.7^{\circ}$ at 24.5° ; sp. gr. 0.8746 at 0° ; 0.862 at 16° ; 0.8547 at 24.5° . Dry hydrogen chloride converts it into a hydrochloride which melts and sublimes at 127° , boils at 204° , and separates from alcohol in large crystals. In alcoholic solution it has rotatory power of $[\alpha]_D = +24.5^{\circ}$ and $[\alpha]_D = +30.5^{\circ}$. By nitric acid and alcohol it is converted into a terpin, $C^{10}H^{16}.2H^2O$.

(4). A terpene agreeing nearly in specific gravity and boiling point with the less volatile terpene of Russian turpentine oil, but optically inactive, is obtained by passing steam through a mixture of terpin crystals (76 pts.) and 50 pts. sulphuric acid diluted with seven or eight times its bulk of water. The terpene then passes over as an oily distillate, which may be purified by boiling it for several hours with a mixture of 1 vol. sulphuric acid and 2 vol. water, then distilling it fractionally and finally over sodium. It boils at 176° – 178° , and has a density of 0.8526 at 15° . It does not appear to be attacked by hydrochloric acid or nitrosyl chloride. When dissolved in hydrochloric and mixed with bromine it is converted into a dibromide, which is resolved by heat into hydrogen bromide and cymene. By oxidation, this hydrocarbon, as well as terpinol, yields, together with other products, para-toluic acid (Tilden, *Chem. Soc. J.* [1878], xxxiii. 250).

(5). From the Swedish wood-tar of *Pinus sylvestris* Atterberg (*Ber.* x. 1202) has obtained two terpenes, which he designates as australene and sylvestrene. The latter has already been described in this volume (p. 1885). The australene agrees very nearly in its physical properties with that obtained from English turpentine oil (v. 920). B. p. 156.5° – 157.5° . Sp. gr. 0.8631 at 16° . Rotatory power $+36.3^{\circ}$. When treated at low temperatures with hydrogen chloride, it yields a solid hydrochloride, which when purified by repeated crystallisation from alcohol, forms feathery crystals melting at 131° ; its rotatory power in alcoholic solution is $+29.8^{\circ}$. It is not attacked by water or by aqueous potash even at 100° , but by hydrogen chloride in ethereal solution it is partly converted into a dihydrochloride. A liquid

compound, probably an *isomeric hydrochloride*, is formed as a bye-product in the preparation of the solid hydrochloride; it appears to be less stable than the latter.

(6). The terpene of clove-oil, after repeated rectification over sodium in a stream of hydrogen, boils at 253.9° (corr.), has a density of 0.905 at 15° , and a vapour-density = 7.7 : hence its molecular formula is $C^{15}H^{24}$ (Church, *Chem. Soc. J.* xxviii. 113).

(7). Nutmeg-oil yields by fractional distillation a terpene, $C^{10}H^{16}$, which boils at 163° – 164° (corr.), and is converted by oxidation with chromic acid mixture into carbonic acid, a volatile acid, probably formic, and a small quantity of terephthalic acid, probably due to admixed cymene. Nitric acid converts it into an acid called myristic acid, which, when dried over sulphuric acid, has the composition $C^{20}H^{30}O^{16}, 2H^{2}O$, together with oxalic acid, and small quantities of toluic and terephthalic acids (C. R. A. Wright, *Chem. Soc. J.* xxvi. 549).

On *Hesperidene*, the terpene of Orange-peel oil, see p. 1028. On the terpene of *Eucalyptus* oil, p. 761.

(8). The terpene of parsley-oil has been examined by E. v. Gerichten (*Ber.* ix. 258). It passes over, on rectifying the oil, as a liquid having a very strong odour of parsley, a density of 0.865 at 12° , and boiling at 164° . Rotatory power for yellow light in a column 100 mm. long = -30.8° . When treated with strong hydrochloric acid, it yielded only a very small quantity of a hydrochloride, and attempts to prepare a terpin from it were unsuccessful. Iodine converts it into a hydrocarbon which yields by oxidation *p*-toluic and *p*-phthalic acids, and is therefore probably cymene.

(9). A solid hydrocarbon, $C^{10}H^{16}$, originally regarded as *ethyl-terpene*, is obtained by the action of sodium and ethyl iodide on camphor chloride (V. Meyer a. Spitzer, *Ber.* ix. 877), also by the action of sodium alone on the same chloride. When purified by distillation and crystallisation from ether it forms a dazzling white crystalline mass, having a camphorous odour, melting at 63.5° and boiling at 153° . It volatilises very quickly on exposure to the air, and is insoluble in water (V. Meyer a. Petri, *Ber.* x. 990; Spitzer, *ibid.* 1034).

(10). A polymeric terpene has been obtained by Jacobsen (*Ber.* ix. 257) from the portion of coal-tar cumene (purified merely by agitation with soda-ley and distillation), which is not attacked (*i.e.* not converted into a sulphonic acid) by sulphuric acid. The greater part of this residual liquid distils between 170° and 180° , another smaller portion between 300° and 330° . The first portion contains a hydrocarbon $C^{10}H^{12}$, boiling under 770 mm. pressure at 170° – 171° . The polymeric terpene is contained in the second portion, and may be separated therefrom by fractional distillation finally over sodium. It is a colourless oily liquid, not miscible in all proportions with alcohol, boiling between 320° and 325° , having a density of 0.885 at 22° , and a refractive index = 1.5009 for the line D. Its formation is probably due to the polymerising action of the strong sulphuric acid on a lower-boiling terpene contained in the crude hydrocarbon.

Compounds of Terpenes with Nitrosyl Chloride, $C^{10}H^{16}(NO)Cl$; and Nitrosoterpenes, $C^{20}H^{32}(NO)$ (Tilden a. Shenstone, *Chem. Soc. J.* xxxi. 554). To prepare the nitrosochlorides, a solution of a terpene in 3 or 4 vol. chloroform (or $\frac{1}{2}$ vol. in the case of terpentine-oil) is saturated at -10° with nitrosyl chloride (p. 1419), care being taken to avoid rise of temperature. The reaction is complete when a sample of the product gives with alcohol a white crystalline precipitate, which is not visibly increased by further action of the nitrosyl chloride. The whole is then stirred into three times its volume of methyl alcohol; the mixture is left to itself for half an hour; and the resulting crystalline precipitate is washed with alcohol and then left to dry in the air. In operating on the terpenes of caraway, bergamot, lemon, and sweet orange, however, it is better to dissolve them in five or six times their volume of methyl alcohol instead of chloroform, keeping the temperature also at -10° . The end of the reaction is then indicated by a slight effervescence. The crude product may be purified, if necessary, by solution in chloroform and precipitation with alcohol.

Australene Nitrosochloride, prepared from American dextrogyrate turpentine-oil boiling at 160° – 161° , and having a rotatory power $[\alpha]_D = +1.75^{\circ}$, melts with decomposition at 103° , and is converted by heating with alcohol and alcoholic potash into a nitrosoterpene, $C^{10}H^{16}NO$, which remains on neutralising the alkaline solution and evaporating; it melts at 129° (corr.)

Terebenthene Nitrosochloride, from French lævogyrate turpentine-oil boiling between 156° and 160° , is very much like the australene compound. The nitrosoterpene obtained from it by the action of alcoholic potash likewise resembles nitroso-australene in melting point and in optical inactivity, but differs from it slightly in crystalline form.

Of the terpenes from *Salvia officinalis* (p. 1771), the one which boils at 158° – 160°

and has a rotatory power $[\alpha]_D = -32.2^\circ$, yields a nitroso-derivative identical with that obtained from australene; whereas the other, boiling at 168° – 176° , and having a rotatory power $[\alpha]_D = -17.7^\circ$, does not yield any analogous nitrosochloride, but is converted, with effervescence, into oily products.

Terpene of *Juniperus communis*, obtained from the portion of the crude oil which boils below 160° , and has a rotatory power $[\alpha]_D = -1^\circ$, yielded a nitrosochloride which was converted by alcoholic potash into a nitrosoterpene melting at 128.5° , and was therefore apparently identical with that prepared from australene.

Inactive terpene, prepared by the action of sulphuric acid either on dextro- or on levogyrate turpentine-oil, and boiling at 156° – 159° , did not yield a crystalline nitrosochloride.

Hesperidene Nitrosochloride (m. p. 103°), prepared from 'essence de Portugal,' boiling at 174° – 175° , is dextrogyrate, $[\alpha]_D = +85.9^\circ$, and yields, with alcoholic potash, a brown oily product, from which a crystalline nitroso-derivative may be obtained. This latter may, however, be prepared in larger quantity by the action of heat on the nitrosochloride itself. For this purpose the nitrosochloride in portions of 1 gram each is fused in test-tubes, and cooled by water immediately after fusion; the resulting honey-like mass, after standing for some hours, is dissolved in alcohol, and the solution is left at rest. It then deposits the nitrosohesperidene in flat prisms, which melt at 71° , and are much more soluble in alcohol than the isomeric compounds above described. This nitroso-compound is sublimable, but polymerises when converted into vapour, so that its vapour-density cannot be ascertained. That it is isomeric and not identical with the nitroso-derivatives of australene and terebenthene is shown by the fact that it is levogyrate ($[\alpha]_D = -36.6^\circ$), although it is prepared from a dextrogyrate terpene. On adding bromine to a solution of nitrosohesperidene in chloroform, and evaporating, the compound $C^{10}H^{15}(NO)Br$ separates out as a semi-crystalline mass.

Terpene from Oil of Caraway, which boils at 178° , and has a rotatory power (100 mm.) equal to $+11^\circ$, forms a nitrosochloride which, when decomposed by heat, yields a nitrosoterpene melting at 71° , and identical with that just described.

Terpene from Bergamot-oil, boiling at 176° , and having a rotatory power (100 mm.) $[\alpha]_D = +75.6^\circ$, yields a nitrosochloride which melts at 98° , and is thereby converted into a nitrosoterpene melting at 71° , which, like nitrosohesperidene, melts at 71° and is levogyrate, but differs from that compound and from the nitroso-derivative obtained from oil of caraway, in crystallising, not in broad flat prisms, but in concentric or parallel groups of very long thin prisms.

Terpene from Lemon-oil yielded only a small quantity of a nitrosochloride, from which no crystalline nitroso-derivative could be obtained. The oil of *Juniperus Sabina* did not yield any derivatives analogous to those above described.

Products of the action of Sulphuric Acid on Terpenes. Deville (*Ann. Chim. Phys.* [1840], lxxv. 37), from an examination of the action of sulphuric acid upon oil of turpentine, inferred that the turpentine is thereby partly converted into 'terebene' (v. 924), an optically inactive liquid hydrocarbon having the same composition and boiling point (about 160°) as the original oil, and partly into colophene (i. 1086), a polymeric hydrocarbon probably of the formula $C^{20}H^{32}$. Riban in 1877 (*Compt. rend.* lxxvi. 1547) confirmed Deville's conclusion that terebene was an isomeride of the terpene from which it was prepared, but showed that the properties ascribed to it by Deville were not those of a pure substance, but of a mixture containing a considerable quantity of cymene; and a similar conclusion was arrived at by Orłowski (*Ber.* vi. 1257), according to whom the product contains more cymene than terebene.

Riban's 'terebene' remained liquid even at -27° , and had practically the same density, boiling point (156°), and refractive index as the terpene from which it was prepared, the only physical difference between them being their behaviour to polarised light; but whereas terpene monohydrochloride was found to melt at 131° – 132° , and to be decomposed only to a very slight extent on prolonged heating with water at 100° , 'terebene' monohydrochloride was found to melt at 125° , and to be very rapidly and completely decomposed by water at 100° , manifesting in this respect the very closest resemblance to the monohydrochloride obtained from inactive camphene, which, however, melts at 145° . Riban observes also that terebene hydrochloride is decomposed even by prolonged washing with cold water, yielding solid camphene and hydrochloric acid, whereas when decomposed by water at 100° , it yields liquid terebene.

The action of sulphuric acid on the terpenes has been further investigated by Armstrong a. Tilden (*Chem. Soc. J.* xxxv. 733), whose results are summarised as follows:

1. The action of sulphuric acid on the terpenes varies both according to the concentration of the acid and the temperature at which the action takes place.

2. The terpenes are most readily deprived of their optical activity by means of concentrated acid acting at an elevated temperature. By the action of the same acid at about 0° , they are chiefly polymerised, the rotatory power of the portion not polymerised being affected only to a comparatively slight extent.

3. Weak sulphuric acid acts very slowly on the terpenes at ordinary temperatures. (1 vol. H^2SO^4 to 1 vol. water), and tends chiefly to polymerise them. By its action at about 80° , however, they are ultimately rendered optically inactive, a considerable proportion remaining unpolymerised. Acids intermediate in concentration between that just mentioned and the undiluted acid appear to furnish intermediate results.

4. The portion of the product of the action of concentrated acid which is volatile with steam does not contain, as Deville, Riban, and Orłowski state, a liquid optically inactive isomeride, boiling at about the same temperature as the parent terpene, neither is cymene the only other constituent of this portion of the product (Riban, Orłowski). So-called terebene, in fact, does not exist, the substance described under this name being merely impure optically inactive camphene; and in the said product it is associated with terpine, the optically inactive liquid isomeride of the terpenes which boils at about 178° , also with cymene and a paraffin-like hydrocarbon of the formula $\text{C}^{10}\text{H}^{20}$. Terpine is the chief constituent of the product in question, and next in amount is camphene; the quantity of cymene is relatively smaller, and that of the hydrocarbon, $\text{C}^{10}\text{H}^{20}$, still smaller.

5. The similar product of the action of acid (1 vol. H^2SO^4 to 1 vol. water) at about 80° does not appear to contain any camphene, but consists principally of terpine; it also contains cymene, the hydrocarbon $\text{C}^{10}\text{H}^{20}$, and a certain amount of oxygenated substance which is but little, if at all, affected by sodium.

6. The portion of the product of the action of sulphuric acid of whatever strength, which does not volatilise with steam—rude colophene—is probably a mixture of polymerides of the form $(\text{C}^{10}\text{H}^{19})_n$. When submitted to distillation, it yields a considerable amount of matter volatile in steam. The product examined by Deville, Riban, and probably by Orłowski, was therefore a mixture of two products.

7. The steam distillate obtained from colophene prepared by the action of acids varying in strength from 2 vol. H^2SO^4 : 1 vol. water to the concentrated acid, resembles in composition the volatile product above described (4), but contains a considerably larger proportion of inactive camphene; it also contains a small quantity of an optically inactive camphol (borneol).

8. The distillate from the colophene obtained by the action of the acid (1 vol. H^2SO^4 : 1 vol. water) on the terpenes, and that from the colophene derived from terpine, contains a relatively much larger amount of cymene and of the hydrocarbon $\text{C}^{10}\text{H}^{20}$ than the distillate from colophene prepared by means of stronger acid. It is doubtful whether it contains camphene.

9. The amount of distillate obtained from colophene prepared under various conditions is subject to considerable variations, the law of which has not yet been ascertained.

10. The small amounts of substances other than those mentioned which are found in the volatile product of the action of sulphuric acid, and also in the colophene distillate, are probably the result of the decomposition of a product of oxidation formed during the prolonged fractional distillation, and in the latter case also during the preparation of the colophene.

11. Probably the best method of preparing pure inactive camphene from the terpenes will be to polymerise the terpene completely by means of an excess of concentrated sulphuric acid at an elevated temperature, and having freed the colophene from cymene, &c., by steam-distillation, to distil it alone, then to fraction the colophene distillate, and treat the fraction collected at about 156° – 160° with hydrochloric acid, and afterwards decompose the camphene hydrochloride so formed by means of an alcoholic solution of potassium hydroxide.

12. Inactive camphene is converted into inactive camphor by oxidation with a mixture of potassium dichromate and sulphuric acid. This inactive camphor yields camphoric acid on oxidation with nitric acid, but the acid prepared in this manner has a much higher melting point than ordinary camphoric acid.

Terpenes and Camphenes have also been obtained from the following sources:

- (1). G. Bouchardat (*Compt. rend.* lxxx. 1446) obtained a *terpine* by heating isoprene, C^8H^8 (iii. 433), at 280° – 290° in sealed tubes from which the air had been displaced by carbon dioxide. The product contained a little unaltered isoprene, a hydrocarbon boiling between 170° – 185° , and higher condensation-products, including a certain quantity of the hydrocarbon $\text{C}^{10}\text{H}^{20}$, but chiefly amorphous colophene. *Terpine*,

which forms the chief constituent of the fraction, passing over from 170° to 185° , and distils, after rectification, between 176° and 181° , has a very strong odour of lemons, resembling also that of isoterbenthene. Sp. gr. = 0.866 at 0° , = 0.853 at 21° . It quickly absorbs oxygen from the air. On passing hydrogen chloride into its ethereal solution, a mixture of two *hydrochlorides* is formed, which remains as an oil when the ether is evaporated off at 20° - 22° . On distilling this mixture under a pressure of 140 mm., a body passes over at 145° , which has nearly the composition $C^{10}H^{16}, HCl$, and remains liquid in a freezing mixture; the temperature then rises quickly to 175° - 180° , whereupon a slight decomposition begins, attended with evolution of hydrochloric acid; and, if the distillation be then interrupted, there remains in the retort a substance which solidifies completely in a freezing mixture, and has the composition $C^{10}H^{16}, 2HCl$. In the surfused state this body may be made to solidify completely by dropping into it a small quantity of the dihydrochloride prepared from turpentine oil, or of the dihydrochloride of caoutchou (1.736). After pressure and recrystallisation from ether, it melts at 49.5° .

(2). A *terpene*, very similar in properties to that just described is obtained in like manner from valerylene, C^8H^8 . After several rectifications, it has a density of 0.848 at 0° and 0.836 at 15° , and distils at about 180° . On passing hydrogen chloride into its solution in a six-fold volume of ether, a *monohydrochloride* is formed, distilling under a pressure of 20 mm. at 115° - 120° , and a *dihydrochloride* boiling under the same pressure at 125° - 140° , and remaining liquid at -14° . The residue contains another dihydrochloride, which cannot be distilled without decomposition even in a vacuum, solidifies at -14° after contact with dihydrochloride of citrene, and then does not liquefy till heated to 25° . These last compounds give a blue colour with ferric chloride. The liquid mono- and di-hydrochloride treated with alcoholic potash, yield terpinol (Bouchardat, *Compt. rend.* lxxxvii. 654).

(3). *Camphenes*.—The name 'camphene,' originally used as a generic term for the hydrocarbons, $C^{10}H^{16}$, was restricted by Berthelot to the solid members which he obtained by the action of certain weak reagents, such as the alkaline stearates, on the hydrochlorides of the terpenes (v. 924). They have since been formed, as already observed, by the action of sulphuric acid on the terpenes, and by other processes. The following have been examined by Riban (*Ann. Chim. Phys.* [5], vi. 353; *Compt. rend.* lxxx. 1307).

Lævorotary Camphene, or *Terecamphene*, was obtained by Berthelot from terebenthene hydrochloride by the action of potassium stearate. Riban prepares it by heating the hydrochloride with about an equal weight of potassium hydroxide and three or four times the same weight of alcohol of 94 per cent. in a closed vessel for seventy-eight hours, treating the product with water, distilling, pressing, and fractionating. It has a faint taste, melts at 45° - 47° , and boils at 156° - 157° (corr.) In the fused state it has at 47.7° a density = 0.8481; at 58.9° = 0.8387; at 79.9° = 0.8211; and at 97.7° = 0.8062, giving for the dilatation-coefficient the formula $D_t = 0.1881 - 0.00839t$. The rotatory power of the camphene in alcoholic solution varies with the degree of dilution. Denoting by e the quantity of alcohol in 100 pts. of the solution, the following values are obtained:

Temp.	e	Rotatory power
13	62.11 p. c.	-51.88°
13	71.50	-51.60
14	80.30	-51.37
14	90.44	-50.99

The rotatory power may be expressed by the equation $[\alpha]_D = 53.80 - 0.3081e$. The *monohydrochloride*, $C^{10}H^{16}, HCl$, is prepared by dissolving 100 pts. of the camphene in 150 pts. absolute alcohol, and saturating the solution with gaseous hydrogen chloride. Rotatory power $[\alpha]_D = +30.25^{\circ}$. It dissociates readily, and must therefore be sublimed in a current of hydrogen chloride; in such an atmosphere it melts at 147° . It is decomposed rather slowly by water at ordinary temperatures, completely by heating for ninety hours with fifty times its weight of water at 100° , the regenerated hydrocarbon being *lævorotary*: $[\alpha]_D = -8.5^{\circ}$.

Inactive camphene was obtained by Berthelot, together with active camphene, from which it could not be separated, by heating terebenthene monohydrochloride with sodium benzoate. This statement is confirmed by Riban, who has also prepared perfectly inactive camphene by heating terebenthene monochloride for eighty hours with twice its weight of sodium or potassium acetate at 170° , distilling, and washing with potash-ley and water to remove acetic acid. Inactive camphene resembles the active modification in all its properties, except the rotatory power. It melts at 470° , boils at 157° (corr.), and yields a monohydrochloride, which is decomposed by water and potash-ley, and melts in an atmosphere of hydrogen chloride at 145° (corr.)

Borneo-camphene, or *Borneene*, originally obtained from *Dryobalanops Camphora* (i. 626), may be formed artificially from common camphor by treating a solution of that substance in toluene with sodium, and the product with carbonic acid, whereby borneol is obtained (vii. 206), and heating the latter with fuming hydrochloric acid at 100°, whereby it is converted into the hydrochloride $C^{10}H^{18}, HCl$, which is optically inactive, resembles ordinary camphene hydrochloride in its properties, melts in an atmosphere of hydrogen chloride at 145°, and is slowly decomposed by water at ordinary temperatures, more quickly at 100°, with formation of borneocamphene.

Conversely, laevogyrate camphene from French turpentine-oil can be converted into camphor by boiling 100 pts. of it for fifteen or sixteen hours in a reflux apparatus with 570 pts. potassium dichromate, 700 sulphuric acid, and 1420 water, acetic acid and apparently a small quantity of butyric acid being formed at the same time. The camphor thus obtained may be freed from traces of camphene by fractional sublimation, rejecting the first sublimate, and from higher-boiling oily bodies by solution in nitric acid, precipitation with water, and sublimation from lime. When thus purified it exhibits the pungent odour and other properties of ordinary camphor, melts at 172° (corr.), and has a laevorotatory power $[\alpha]_D = -13.7^\circ$, opposite therefore in direction to that of ordinary camphor. The camphoric acid formed from it is also laevogyrate; $[\alpha]_D = -6.5^\circ$, and melts at 197°–198° (corr.); camphiric acid from common camphor melts at 187° (corr.)

TERPENYLIC ACID, $C^8H^{12}O^4$ (C. Hempel, *Ber.* vii. 357). This acid is formed by oxidising terpin or turpentine-oil with a quantity of chromic acid not sufficient for complete oxidation; and in like manner, according to Sauer (*ibid.* x. 522), from terebene (impure inactive camphene) and the terpene of lemon-oil. It is obtained at first in the form of a syrup resembling glycerol, but on leaving its concentrated solution for some time exposed to the air, it solidifies almost completely, and is easily obtained pure by pressure and recrystallisation. It is very soluble in water, and crystallises therefrom in radiate groups of colourless laminae, having the composition $C^8H^{12}O^4 + H^2O$, which give off their water in the exsiccator, and crumble to a powder melting at 90° (Hempel). It is resolved by heat into carbon dioxide and teracrylic acid, $C^8H^{12}O^2$ (Krafft, p. 1900).

Terpenylic acid is monobasic. Its salts are so soluble that even a tolerably concentrated solution of the ammonium salt forms no precipitate with any of the ordinary metals. The *silver salt*, $C^8H^{11}O^4Ag$, separates from a hot concentrated solution as a white loosely coherent crystalline mass, which does not blacken at 90° or on exposure to light. The *copper salt*, $(C^8H^{11}O^4)^2Ca$, separates from solution on spontaneous evaporation in small well-defined dark-blue crystals. The *ethylic ether*, which melts at 36°–38°, and boils almost without decomposition at about 300°, is not attacked by acetyl chloride at 100°: consequently terpenylic acid does not contain any hydroxyl-groups. According to its formula it should be the next homologue of terebic acid, to which indeed it exhibits a certain degree of analogy (Hempel). When treated with barium hydrate, it is converted into the barium salt of diaterpenylic acid, $C^8H^{12}BaO^5$. The ethylic ether of this acid is solid (E. Sauer, *Ber.* x. 522; Krafft, *ibid.* 1660).

TERPIN and TERPINOL (v. 923). Tilden (*Chem. Soc. J.* xxxiii. 247) prepares terpin, $C^{10}H^{20}O$, by leaving a mixture of 1 vol. nitric acid (sp. gr. 1.4), 1 vol. methyl alcohol, and 2½ vol. pure turpentine-oil (either French or American) to itself for two days, then pouring it into an open dish, and gradually pouring upon it, at intervals of two days, small quantities of methyl alcohol. Orange terpenes thus treated do not yield terpin. Contrary to the statements of former observers, Tilden finds that terpinol (prepared by the action of hydrochloric acid upon terpin) boils between 205°–215°, and has the composition $C^{10}H^{18}O$ or $C^{20}H^{36}O^2$. Accordingly terpin may be represented by the rational formula $C^{10}H^{18}(OH)^2$, and terpinol by $C^{10}H^{18} \begin{smallmatrix} \diagup O \diagdown \end{smallmatrix} C^8H^{18}$. The latter treated with dry hydrogen chloride yields the *di-hydrochloride of turpentine oil*, $C^{10}H^{18}, 2HCl$, in crystals which melt at 50°, and are converted by sodium ethylate at the boiling heat into a mixture of the compounds $C^{10}H^{18} \begin{smallmatrix} \diagup OC^2H^5 \diagdown \\ \diagup Cl \diagdown \end{smallmatrix}$, and $C^{10}H^{18}(OC^2H^5)^2$. An alcoholic solution of terpinol mixed with *hydrochloric acid* gradually deposits terpin.

Terpin treated with dilute sulphuric acid (1 pt. H^2SO^4 to 7 or 8 pts. water) yields, together with a small quantity of terpinol, a terpene apparently identical with one of the terpenes obtained from Russian turpentine-oil (p. 1902).

TETRABENZOYL-DIAMIDOPHENOLS. See PHENOLS, AMIDO- (pp. 1522, 1523).

TETRABENZOYL-MORPHINE. See MORPHINE (p. 1340).

TETRABROMACETIC ETHER, $C^4H^4Br^4O^2$, is formed by the action of bromine at 160° on the dibromacetic ether, $C^4H^2Br^2O^2$, which is obtained by heating ethylidene acetoxychloride, $CH^2.CH(OC^2H^3O)Cl$, with bromine at $102^\circ-103^\circ$. When freed from absorbed hydrogen bromide by heating in a stream of carbon dioxide, it forms an oily liquid which fumes strongly in the air, and decomposes when distilled. It is also decomposed by water and alcohol, yielding products which reduce an ammoniacal silver solution. Heated with bromine in sealed tubes at 170° , it is converted into pentabromacetic ether, $C^4H^2Br^5O^2$, probably $CH^2Br.CO.OCBBr^2.CHBr^2$, which is a liquid, fuming very slightly in the air, and boiling without decomposition at $175^\circ-177^\circ$. With water it yields a product of decomposition which does not reduce ammoniacal silver-solution. With alcohol it yields 1 mol. monobrom- and 1 mol. dibromacetic ether (b. p. 194°), together with hydrogen bromide and traces of brominated acetic acid, but no silver-reducing substance. It is different from the pentabromacetic ether obtained by heating ethyl acetate with bromine (p. 11). Heated with excess of bromine at a very high temperature, it is converted into hexbromacetic ether, $C^4H^2Br^6O^2$, a liquid boiling almost without decomposition at $195^\circ-198^\circ$ (F. Kessel, *Ber.* xi. 1917).

TETRABROMALIZARIN, $C^{14}H^4Br^4O^2$, is obtained by heating alizarin with excess of bromine at 180° , and may be purified by repeatedly crystallising the product from glacial acetic acid, in which it dissolves with rust-brown colour. It is nearly insoluble in water and in alcohol. In alkalis and in strong sulphuric acid it dissolves with dark red to brown-red colour, and the solutions yield brown-red precipitates with lime-water, baryta-water, and alcoholic lead acetate. It melts at a high temperature, and sublimes as a light brown deposit, with considerable carbonisation. When heated with iodine bromide it is decomposed, partially at 200° , completely at 250° , into carbon dioxide, perbromethane, and pentabromobenzene (Diehl, *Ber.* xi. 187).

TETRABROMANILINE, $C^6HBr^4.NH^2$ [1 : 2 : 4 : 6, NH^2 in 1]. See BENZENES, BROMAMIDO- (p. 195).

TETRABROMANTHRACENE TETRABROMIDE, $C^{14}H^2Br^4$, Br⁴ (p. 1499).

TETRABROMAZOPHENOLS. See PHENOLDIAZINS in the ADDENDA.

TETRABROM-ETHANE or **TETRABROMETHYLENE HYDRIDE**, $C^2H^2Br^4$, produced by the action of bromine on dibromosuccinic acid at 170° , is a crystalline body, isomeric with acetylene tetrabromide or dibromomethylene dibromide, formed by the action of bromine on a saturated solution of acetylene in absolute alcohol. Tetrabromethane melts at 54.5° , and boils with partial decomposition at 206° ; whereas acetylene bromide is liquid at ordinary temperatures, and is resolved at 190° into HBr and tribromomethylene (Bourgoin, *Ann. Chim. Phys.* [5], iii. 421); compare p. 35.

The same tetrabromethane appears to be formed, together with other products, by heating ethylidene oxychloride with bromine in sealed tubes till carbonisation takes place. The syrupy product is resolved by distillation into three portions, the second of which, passing over between 190° and 240° , has the composition $C^2H^2Br^4$. It is insoluble in water, dissolves easily in ether, alcohol, and carbon sulphide, crystallises therefrom in nacreous scales, melts at 52° , and boils at 220° (Kessel, *Ber.* x. 1667).

TETRABROM-ETHYLACETYLENE, $C^4H^2Br^4$, obtained by the action of bromine on ethyl-acetylene, $CH^3.CH^2.C\equiv CH$ (produced by the action of PCl^3 on methylethyl ketone, and treatment of the product with alcoholic potash), is a crystalline body soluble in alcohol, ether, and carbon sulphide, subliming without fusion at 105° (Braylants, *Ber.* viii. 410).

TETRABROM-ETHYLENE, C^2Br^4 , is formed, together with hexbromethane, by gradually heating ethyl iodide with bromine to 250° . It boils at 53° (Merz & Weith, *Ber.* xi. 2235).

TETRABROM-ETHYLENE HYDRIDE, syn. with TETRABROMETHANE.

TETRABROM-ETHYL OXIDE, $C^4H^2Br^4O$ — $(CH^2Br.CHBr)^2O$, obtained by saturating ethylidene oxychloride with bromine at $115^\circ-120^\circ$, is a faintly-yellowish syrupy liquid, which fumes in the air and is decomposed by water (Kessel, *Ber.* x. 1667).

TETRABROMOBENZENES, $C^6H^2Br^4$ (p. 169).

TETRABROMOBENZENESULPHONIC ACID, $C^6HBr^4.SO^3H$. See p. 243.

TETRABROMOBUTYRIC ACID, $C^4H^4Br^4O^2$ (m. p. 120° – 130°), is formed, together with other products, by heating mucobromic acid, $C^1H^2Br^2O^2$, with bromine and water at 120° – 130° (vii. 828).

TETRABROMOCAPROIC ACID, $C^6H^4Br^4O^4$. Identical with **SORBIC TETRABROMIDE** (p. 1897).

TETRABROMOCARBAZOL, $C^{12}H^3Br^4N$. A product having nearly this composition is formed by the action of bromine on carbazol (vii. 253), either in the dry state or dissolved in carbon sulphide (Graebe a. Glaser, *Liebig's Annalen*, clxiii. 343).

TETRABROMOCATECHOL or **TETRABROMOPYROCATECHIN**, $C^8H^2Br^4O^2$. See p. 1709.

TETRABROMOCORALLIN-PHTHALEIN, $C^{20}H^{10}Br^4O^4$. See **CORALLIN**, under **ROSAURIN** (p. 1764).

TETRABROMODECANE, $C^{10}H^{18}Br^4$, is formed by direct combination of bromine with menthene, $C^{10}H^{18}$ (iii. 880), and is resolved by heat into hydrogen bromide and cymene: $C^{10}H^{18}Br^4 = 4HBr + C^{10}H^{14}$ (Beckett a. Wright, *Rep. Br. Assoc.* 1875, [2 Abth.], 38).

TETRABROMODIHYDROXYDIPHENYLMETHANE, $C^{13}H^4Br^4O^2$, is formed on adding bromine-water to a hot aqueous solution of dihydroxyphenylmethane, $CH^2(C^6H^4OH)^2$, [produced by the action of melting potash on the potassium salt of diphenylmethanedisulphonic acid (p. 684)], and separates in the form of a white precipitate. When purified it forms laminæ having a roddish shimmer, soluble in alcohol and in ether, insoluble in water, melting at 225° , and decomposing at a higher temperature. Its *hydrobromide*, $C^{13}H^4Br^4O^2$, may be prepared by slowly dropping bromine into an ethereal solution of dihydroxydiphenylmethane, and leaving the resulting solution to evaporate below 0° . The yellow crystalline masses thus obtained decompose on exposure to the air, with separation of hydrogen bromide, and dissolve in alcohol with formation of ethyl bromide (C. Beck, *Ber.* x. 1837).

TETRABROMODIPHENYLAMINE, $NH(C^6H^3Br^2)^2$. See **PHENYLAMINES** (p. 1549).

TETRABROMOFLUORENE, $C^{13}H^0O^4$, resembles the tribromo-derivative (q.v.).

TETRABROMOFLUORESCEIN, or **EOSIN**, $C^{20}H^2Br^4O^5$. See **PHTHALEINS** (p. 1609). The following observations on eosin and allied colouring matters have been made by Bindschedler a. Busch (*Chem. News*, xxxviii. 226). *Yellowish Eosin*, soluble in water (*sodium-tetrabromofluorescein*), is obtained by adding 1.1 kg. bromine, with agitation to 1 kg. finely pulverised fluorescein suspended in ten litres of alcohol; the fluorescein already partially brominated then passes into solution, and is again gradually treated with 1.1 kg. bromine, each drop of which produces a crystalline precipitate of tetrabromofluorescein. The precipitate is left to settle, separated by decantation, and washed, first with alcohol, then with water, till the liquid runs away perfectly neutral. The product is then dissolved in caustic soda, and the solution, which must not have an alkaline reaction, is evaporated to crystallisation. *Bluish Eosin*, soluble in water (*sodium-tetraiodofluorescein*), is obtained by adding the calculated quantity of iodine dissolved in alkali to an alkaline solution of fluorescein, and then adding an acid, whereby a crystalline precipitate is formed; and, on dissolving this precipitate in caustic soda and evaporating, the commercial product is obtained. Its aqueous solution does not exhibit any sign of fluorescence. *Safrosin*, soluble in water, is a sodium salt of nitrated eosin, and is obtained on mixing 9 kg. eosin in alkaline solution with 8 kg. sodium nitrate, heating the mixture to the boiling point, and then adding 15 kg. sulphuric acid of 66° B. The resulting precipitate, which has the colour of manganous sulphide, is washed, and dissolved in caustic soda, and the solution is evaporated. The colouring matter thus obtained dyes wool of a deeper and more bluish-red than eosin, and yields with naphthalene-orange a good substitute for cochineal.

Eosin soluble in alcohol exhibits a greater variety of tints, like those of flowers, than eosin soluble in water, and is more permanent. It is obtained by heating 5 kg. eosin with 15 litres of pure methyl alcohol and 9 kg. sulphuric acid of 66° B. for four hours in the water-bath. The resulting methyl-derivative of tetrabromofluorescein is purified by pouring it into a large quantity of water, filtering and washing, and is sent into the market in the form of a potassium salt. In the dried state it is soluble in a mixture of equal parts of water and alcohol, the solution exhibiting a splendid fluorescence. The *ethyl*-derivatives prepared in like manner have a somewhat fainter

yellowish colour. For further details see *Die Chemische Industrie redigirt von Dr. E. Jacobsen*, Berlin, 1878, 370; also *Monit. Scientif.* [3], viii. 1169).

TETRABROMOHYDROXYPIPERHYDRONIC ACID, $C^{12}H^{10}Br^4O^5$. See PIPERIC ACID (p. 1632).

TETRABROMOLEUCROSAURIN. See ROSAURIN (p. 1763).

TETRABROMOMETHYLFLUORESCHEIN (p. 1909).

TETRABROMONAPHTHOIC ACIDS, $C^{10}H^8Br^4COOH$. See NAPHTHALENE-CARBOXYLIC ACIDS (p. 1360).

TETRABROMOPHENANTHRENE, $C^{14}H^6Br^4$ (p. 1514).

TETRABROMOPHENOL-PHTHALEIN, $C^{20}H^{10}Br^4O^4$, and **-PHTHALEIN**, $C^{20}H^{10}Br^4O^4$ (pp. 1604-1605).

TETRABROMOPIPERHYDRONIC ACID, $C^{12}H^{10}Br^4O^4$. See PIPERIC ACID (p. 1633).

TETRABROMORCINOLPHTHALEIN, $C^{22}H^{12}Br^4O^5$, formed by adding bromine to a boiling solution of orcinol-phthalein (p. 1612) in glacial acetic acid, is a faintly yellowish crystalline powder, only sparingly soluble in nearly all solvents, but dissolving readily and with dark brown colour in dilute alkalis (E. Fischer, *Ber.* vii. 1214).

TETRABROMOTRUTHIN, p. 1445.

TETRABROMOROSAURIN, $C^{20}H^{12}Br^4O^5$. See ROSAURIN (p. 1763).

TETRACETYL-BRAZILIN, $C^{16}H^{10}(C^2H^3O)^4O^5$ (p. 348).

TETRACETYL-CONIFERIN, $C^{16}H^{18}(C^2H^3O)^4O^6$, is obtained by digesting coniferin (p. 553) with acetic anhydride at 100° , and precipitating with water, and separates as a white crystalline precipitate, which softens at 90° , and melts at 125° , 126° to a clear liquid solidifying to a transparent mass on cooling. It is insoluble in cold, slightly soluble in hot water, dissolves with moderate facility in cold alcohol and ether, very easily in boiling alcohol (Tiemann u. Naganosi Nagai, *Ber.* viii. 1140).

TETRACETYL-CODEINE, $C^{72}H^{80}(C^2H^3O)^4N^4O^{12}$. See CODEINE, under MORPHINE (p. 1340).

TETRACETYL-MORPHINE, $C^{34}H^{34}(C^2H^3O)^4N^2O^6$ (vii. 820).

TETRACETYL-QUINATE, ETHYLIC, $C^6H^7(OC^2H^3O)^4COOC^2H^5$. See QUINIC ACID (p. 1734).

TETRACETYL-SULPHOTANNIC ACID, $C^{16}H^{16}S^2O^{12}$. See TANNIC ACID (p. 1889).

TETRACETYL-TETRABROMO-DIIMIDOPHENOL-PHTHALEIN, $C^{22}H^{20}Br^4N^2O^6$. See PHTHALEINS (p. 1605).

TETRABUTYRYL-MORPHINE, $C^{64}H^{64}(C^4H^7O)^4N^2O^6$ (vii. 820).

TETRACHLORACETONE, $C^3H^2Cl^4O$. See ACETONE (p. 26).

TETRACHLORALIZARIN, $C^{14}H^4Cl^4O^4$, is prepared by heating alizarin at 100° in a sealed tube with antimony pentachloride, boiling the dark brown product with acid, dissolving it in soda-ley, precipitating with an acid, and finally dissolving it in a mixture of benzene and alcohol, from which it separates in the form of a red-brown crystalline powder. It begins to melt at 260° , but is almost entirely carbonised at a higher temperature. It is insoluble in water, but dissolves readily in glacial acetic acid, benzene, chloroform, carbon sulphide, and hot alcohol. Soda-ley dissolves it with brown colour. It does not dye mordants (Diehl, *Ber.* xi. 187).

TETRACHLORANILINES, $C^6H^3Cl^4N$. See PHENYLAMINES (p. 549).

TETRACHLORANTHRACENE, $C^{14}H^4Cl^4$, is formed by the action of alcoholic potash on dichloranthracene dichloride, $C^{14}H^8Cl^2Cl^4$ (Diehl, *Ber.* xi. 173). See also vi. 179.

TETRACHLORANTHRAQUINONE, $C^{14}H^4Cl^4O^2$, is obtained by heating dichloranthraquinone for some time in a sealed tube at 200° - 220° with six times its weight of antimony pentachloride, and may be separated from adhering trichloranthraquinone by exhausting the crude product with hot glacial acetic acid, and fractional crystallisation, and finally purified by sublimation. It crystallises in yellow needles melting without decomposition at 320° - 330° , easily soluble in chloroform, toluene, carbon sulphide, and boiling glacial acetic acid (Diehl, *Ber.* xi. 179).

TETRACHLORAZOXYBENZENE, $\begin{matrix} \text{C}^6\text{H}^4\text{Cl}^2\text{N} \\ | \\ \text{C}^6\text{H}^4\text{Cl}^2\text{N} \end{matrix} \text{O}$. This compound is

known in two modifications, one of which is formed by heating [1 : 3 : 4] nitro-dichlorobenzene, $\text{C}^6\text{H}^3\text{NO}_2\text{H}^2\text{Cl}^2$ (m. p. 545°), with alcoholic potash, the solution on cooling depositing a dark-coloured mass, from which the tetrachlorazoxybenzene may be obtained by washing with cold alcohol and boiling with carbon sulphide, which dissolves the azoxy-compound and leaves a brown powder. Pure tetrachlorazoxybenzene crystallises in very small light-yellow needles melting at 141.5° ; soluble in chloroform, benzene, and glacial acetic acid. Strong sulphuric acid dissolves it with red colour (Laubenheimer, *Ber.* vii. 1600; viii. 1626).

The second modification, formed by the action of alcoholic potassium hydrosulphide on symmetrical or [1 : 3 : 5] dichloronitrobenzene, melts at 171° – 172° (Beilstein a. Kurbatow, *Ber.* xi. 514).

TETRACHLOROBENZENES, $\text{C}^6\text{H}^2\text{Cl}^4$ (p. 173). The consecutive modification may be obtained from nitrotrichlorobenzene, $\text{C}^6\text{H}^3\text{Cl}^3\text{NO}_2$, by reduction and subsequent replacement of the amido-group by chlorine.

TETRACHLOROBENZOIC ACID, $\text{C}^6\text{HCl}^4\text{CO}_2\text{H}$, is formed by heating orthochlorobenzoic acid with six times its weight of antimony pentachloride for three or four hours at 230° . Its barium salt, after repeated crystallisation from alcohol, forms beautiful needles containing $(\text{C}^6\text{HCl}^4\text{O}_2)^2\text{Ba} + 4\text{H}_2\text{O}$ (Beilstein, *Ber.* viii. 435).

TETRACHLOROBILIRUBIN. See BILE-PIGMENTS (p. 325).

TETRACHLOROCARBAZOL, $\text{C}^{12}\text{H}^2\text{Cl}^4\text{N}$, is formed, together with less highly chlorinated products, by passing chlorine into a solution of carbazol in carbon sulphide (Graebe a. Glaser, *Liebig's Annalen*, cxliii. 343).

TETRACHLOROCUMARIN, $\text{C}^9\text{H}^2\text{Cl}^4\text{O}^2$, is obtained by passing chlorine into a solution of coumarin and iodine in carbon tetrachloride. It crystallises from alcohol in white needles melting at 144° – 145° (Perkin, *Chem. Soc. J.* xxv. 37).

TETRACHLORODIETHYL-GLYCOL,

$\text{C}^6\text{H}^4\text{Cl}^4\text{O}^2 = \text{CCl}_3\text{—CH} \begin{matrix} \text{O} \\ \diagup \quad \diagdown \\ \text{Cl} \end{matrix} \text{—CH}_2\text{—CH}_2\text{—} \begin{matrix} \text{O} \\ \diagdown \quad \diagup \\ \text{Cl} \end{matrix} \text{—CH—CCl}_3$, formed by the action of phosphorus pentachloride on the compound of glycol and chloral, is a viscid liquid, having a density of 1.73 at 17° , insoluble in water, and decomposing when distilled (L. Henry, *Ber.* vii. 762).

TETRACHLORODIMETHYLQUINOL, $\text{C}^6\text{Cl}^4(\text{OCH}^3)^2$. See QUINOL (p. 1738).

TETRACHLORODIPHENYLAMINE, $\text{NH}(\text{CH}^6\text{Cl}^2)^2$. See DIPHENYLAMINE (pp. 200, 1549).

TETRACHLORONAPHTHALENE, $\text{C}^{10}\text{H}^4\text{Cl}^4$ (p. 1350).

TETRACHLORONITROBENZENE, $\text{C}^6\text{H}(\text{NO}_2)\text{Cl}^4$, crystallising in needles, at 20° – 22° , is obtained by the action of strong nitric acid on symmetrical tetrachlorobenzene, [1 : 2 : 4 : 5]. It dissolves readily in carbon sulphide, benzene, and hot alcohol (Beilstein a. Kurbatow, *Ber.* ix. 679).

TETRACHLOROPHENANTHRENE, $\text{C}^{14}\text{H}^4\text{Cl}^4$. See PHENANTHRENE (p. 1515).

TETRACODEINE, $\text{C}^{144}\text{H}^{168}\text{N}^8\text{O}^{24}$. See CODEINE (vii. 372).

TETRADYMIT. Native Telluride of Bismuth (p. 1897).

TETRAHEDRITE. *Fahl-ore*. A number of tetrahedrites and other sulphur salts from Sweden have been examined by N. Nilson (*Zeitschr. Kryst.* i. 417):—

1–5. Tetrahedrite agreeing with the formula $2(4\text{RS}^2\text{Sb}^2\text{S}^3) + 4\text{R}'^2\text{S}^2\text{Sb}^2\text{S}^3$. This mineral was formerly regarded as identical with Svanberg's *aphthonite* from Gärdgön, Wermland (v. 729); but Nilson shows that Svanberg's original analysis of *aphthonite* (No 6), from which he deduced the formula $7\text{RS}^2\text{Sb}^2\text{S}^3$ (in which RS must be supposed to denote partly CuS in place of Cu²S), agrees equally well with the formula $2(4\text{Cu}^2\text{S}^2\text{Sb}^2\text{S}^3) + 4\text{ZnS}^2\text{Sb}^2\text{S}^3$, in which 1 Cu is replaced by 1 Ag, and 1 Zn by 1 Fe. The values calculated from this formula, $\text{Cu}^{15}\text{AgZn}^3\text{FeSb}^4\text{S}^{27}$, are given under No. 7. Nilson further observes that Atterberg's analysis of a mixture of metallic bismuth with a sulphur-salt (No. 8), gives for the latter the formula $3\text{RS}^2\text{Sb}^2\text{S}^3$, in which $3\text{R} = 2\text{Pb} + 1\text{Fe}$ (No. 9), supposing the mineral to contain 36.81 per cent. metallic

bismuth. Lastly Nilson reproduces Lundström's analyses (No. 10) of the mineral called *Bjelkite* by Nordenskiöld, the composition of which is represented by the formula $\text{FePb}^2\text{Bi}^2\text{S}^4 = 3\text{RS}, \text{Bi}^2\text{S}^2$. The only other sulphur salts found in Sweden are *Geocronite*, *Boulangierite*, and *Kobellite*.

	S	Sb	Bi	Pb	Fe	Cu	Ag	Zn	
1.	23.56	26.85	—	—	0.95	41.06	6.16	0.71	= 99.29
2.	23.58	26.96	—	—	0.81	not det.	5.78	0.54	—
3.	23.47	26.70	—	—	0.83*	35.70	6.07	5.42	= 98.19
4.	24.16	27.48	—	—	0.79	36.53	6.15	4.73	= 99.84
5.	22.78	26.13	—	—	2.84	36.96	6.07	4.72	= 99.50
6.	30.35	25.01	—	—	1.82 ⁽¹⁾	33.23	3.12	6.47	= 100
7.	29.72	25.18	—	—	1.92 ⁽¹⁾	32.76	3.71	6.71	= 100
8.	10.39	—	68.40	17.90	1.52	—	—	—	= 100.96 ⁽²⁾
9.	16.61	—	50.50	28.62	2.43	—	—	—	= 100 ⁽³⁾
10.	17.83	—	39.40	37.64	5.13	—	—	—	= 100
11.	17.74	—	38.82	38.26	5.18	—	—	—	= 100

(¹) Containing Cobalt. (²) Including 1.15 per cent. Se and 1.60 per cent. gangue. (³) Including 1.84 per cent. Se.

Fahl-ore from Brixlegg crystallised in rhombic dodecahedrons, and imbedded in heavy spar, has been analysed (1) by G. Untchj (*Jahrb. f. Min.* 1873, 80) and (2) by F. Becke (*Min. Mittl.* 1877, 273) with the following results:

S	Sb	As	Bi	Cu	Zn	Ag	Fe
25.59	20.44	6.96	—	39.37	4.43	—	3.21 = 100
23.0	17.0	11.2	0.4	40.2	3.0	0.9	4.2 = 99.9

Unlike most rhombic-dodecahedral fahl-ores, therefore, it is *not* a mercury fahl-ore.

The decomposition-products of the mercury fahl-ore of Maschellandsberg in the Pfalz have been examined by F. Sandberger (*Jahrb. f. Min.* 1872, 646). This mineral (sp. gr. 5.095) contains, according to an analysis by Oellacher:

S	As	Sb	Bi	Ca	Hg	Fe	Co	Zn	Gangue
21.90	0.31	23.45	1.57	32.19	17.32	1.41	0.23	0.10	1.39 = 99.87

Hence its proximate constitution may be calculated as:

As ² S ³	Sb ² S ³	Bi ² S ³	Cu ² S	HgS	FeS	CoS	ZnS
0.51	32.81	1.93	40.31	20.09	2.22	0.35	0.15

By decomposition the fahl-ore is converted into a light, lead-grey, porous mass, which qualitative analysis shows to consist of Cu^2S . The material filling up the cavities consists, according to an analysis by E. Prior, of 24.70 per cent. HgS , 46.85 Cu^2S , 1.04 insoluble residue, and 27.41 FeCO_3 (determined by difference). The iron-carbonate is evidently an accidental admixture, and the ratio of the cinnabar to the copper-glance (1 : 2 in the fahl-ore) is scarcely altered by the decomposition (1 : 1.9 in the product); but the sulphur-acids have been removed (probably by barium sulphide). The ultimate product of the decomposition is a mixture of malachite, stibite, and cinnabar.

Antimony fahl-ore, crystallised in tetrahedrons and in crystalline crusts 3 mm. thick, from a well-shaft at Bourbonne-les-Bains, has been analysed by G. Krause (*Arch. Pharm.* [3], vi. 409) with the following result:

S	Sb	As	Cu	Fe	Ni	Sn	Sp. gr.
23.44	26.40	trace	43.20	4.00	strong	traces	= 97.04 5.137

On the Crystallography of Fahl-ore and its regular intergrowth with Copper-pyrites, see Sadebeck (*Zeitschr. geol. Ges.* xxiv. 173, 427; *Jahrb. f. Min.* 1873, 801; further, *Ann. Phys. Chem.* [2], v. 578).

TETRAHYDROISOLEPIDIN, $\text{C}^8\text{H}^{12}\text{O}$. See LEPIDIN (p. 1177).

TETRAIODHYDROXSULPHOBENZIDE, $\text{SO}^2[\text{C}^6\text{H}^4\text{I}^2(\text{OH})]^2$. See OXSULPHOBENZIDE (p. 1475).

TETRAIODODIPHENYL DIOXIDE, $\left\{ \begin{array}{c} \text{C}^6\text{H}^4\text{I}^2\text{O} \\ \text{C}^6\text{H}^4\text{I}^2\text{O} \end{array} \right\}$, apparently identical with

the compound $\text{C}^8\text{H}^4\text{I}^4\text{O}$, which Lautemann obtained by the action of alkalis on triiodosalicylic acid (v. 158), is formed by the action of iodine on phenol in alkaline solution. To prepare it, a boiling solution of 300 g. sodium carbonate in a litre of

TETRAMETHYL-ALLENE—TETRAMETHYLETHYLENE. 1913

water is mixed with 10 g. phenol, and then with 70–75 g. iodine (dissolved in a solution containing 45 g. potassium iodide); 30 g. more sodium carbonate are added to remove excess of iodine; the hot solution is filtered; and the red precipitate is washed first with water, then with alcohol, and repeatedly crystallised from carbon sulphide, in which it dissolves easily with deep red colour. It is insoluble in ether, benzene, and chloroform. By sodium-amalgam it is converted into di-iodo-diquinol, $C^6H^4IOH.C^6H^4IOH$; by sulphurous acid into tetraiodo-diquinol, $C^6H^4IOH.C^6H^4IOH$ (Kämmerer & Benzinger, *Ber.* xi. 357).

TETRA-IODOFLUORESCIN. See p. 1909.

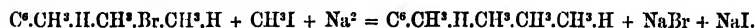
TETRA-ISOBUTYLAMMONIUM IODIDE. See TRI-ISOBUTYLAMINE.

TETRAMETHYL-ALLENE, $C^3H^{12} = (CH^3)_2C = C = C(CH^3)_2$, is formed by the action of alcoholic potash on the chloride $C^3H^{12}Cl$, which is produced by treating di-isopropyl ketone or isobutyron, $(CH^3)_2CH.CO.CH(CH^3)_2$, with phosphorus pentachloride. This hydrocarbon is a liquid having a very disagreeable odour, boiling at about 70° , and forming an addition-product with bromine. The chloride, $C^3H^{12}Cl$, is a colourless liquid which boils between 118° and 120° , and has a density of 0.9513 at 9° . The crude product of the action of phosphorus pentachloride on isobutyron also contains a dichloride, $C^3H^{12}Cl_2$, which, however, is converted during distillation into the monochloride (L. Henry, *Ber.* viii. 400).

TETRAMETHYLAMMONIUM, $N(CH^3)^4$. According to Rabuteau (*Monit. scient.* [3], iii. 451), the salts of this base, and those of tetramethylammonium, exert a poisonous action on the animal organism similar to that of curare.

The chloride, $N(CH^3)^4Cl$, is formed, together with trimethylamine hydrochloride, methylamine, and methyl oxide, by heating sal-ammoniac with excess of methyl alcohol (Weith, *Ber.* viii. 458). The iodide, well crystallised, has a density of 1.827 at 17° , and 1.831 at 19.5° (Clarke, *Sill. Am. J.* [3], xvi. 401). It is perfectly stable at high temperatures (Hofmann, *Ber.* vii. 526). On tetramethylammonium ferrocyanide, $FeCy_4[(CH^3)^4N]^{+} + 13H^2O$, see METHYLAMINES (p. 1306). E. Fischer (*Liebigs Annalen*, xc. 134) represents it by the formula $FeCy_2H^2[(CH^3)^4N]^2 + 2H^2O$.

TETRAMETHYLBENZENES, $C^{10}H^{14} = C^6H^2(CH^3)^4$. On symmetrical tetramethylbenzene or durenol, $[1 : 2 : 4 : 5]$, see pp. 695, 1444. Another modification, distinguished as β , is produced by heating a solution of 25 g. monobromomesitylene and 40 g. methyl iodide in benzene with 14 g. sodium: hence it must be the unsymmetrical modification $[1 : 3 : 4 : 5]$:

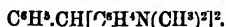


When purified by fractional distillation over sodium, it is a liquid which has a faint pleasant aromatic odour, does not solidify in a freezing mixture, boils at 192° – 194° (Durenol is solid at ordinary temperatures, melts at 79° – 80° , boils at 189° – 191°). Bromine in excess converts it, with violent reaction, into a dibromo-derivative, $C^{10}H^{12}Br^2$, which dissolves sparingly in cold, much more readily in boiling alcohol, and separates therefrom in shining needles melting at 199° (Jannasch, *Ber.* viii. 355).

TETRAMETHYLDIAMIDAZOXYBENZENE, $C^{12}H^4(CH^3)^4(NH^2)^2N^2O$, is formed by the action of alcoholic potash on the hydrochloride of nitrosodimethylaniline, and crystallises in brown shining needles (p. 1309).

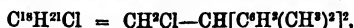
TETRAMETHYL - DIAMIDOBENZOPHENONE, $CO[C^6H^4N(CH^3)^2]^2$. See KETONES (p. 1153).

TETRAMETHYLDIAMIDOTRIPHENYLMETHANE,



This constitution is assigned by O. Fischer (*Ber.* xi. 950) to the condensation-product formed by the action of zinc chloride on a mixture of benzaldehyde and dimethylaniline (p. 1308). The alcoholic solutions of its salts are converted by oxidation into blue-green colouring matters. Its hexnitro-derivative forms golden-yellow needles melting at 200° .

TETRAMETHYLDIPHENYLCHLORETHANE,

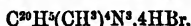


is formed by the action of sulphuric acid on a mixture of xylene and dichlorethyl oxide, and is converted by dry distillation into tetramethylstilbene, $C^{18}H^{20}$.

TETRAMETHYLETHYLENE, $(CH^3)_2C = C(CH^3)_2$. See HEXYLENES (p. 1036).

TETRAMETHYLMETHANE, $C^8H^{12} = C(CH^3)^4$. This pentane is formed by the action of zinc-methyl on tertiary butyl iodide, $C(CH^3)_3I$, and on dichloropropane, $CH^2.CCl^2.CH^3$ (vii. 63, 1037; viii. 1499).

TETRAMETHYL-ROSANILINE HYDROBROMIDE,



is formed, according to Brunner a. Brandenburg, by the action of bromine on dimethylaniline (p. 1305).

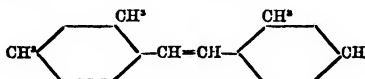
TETRAMETHYL-RUFIGALLOL, $C^{14}H^4(CH^3)^4O^2$. See RUFIGALLOL (p. 1768).

TETRAMETHYL-STILBENE, $C^{18}H^{20} = (CH^3)^2C^6H^8.CH=CH.C^6H^8(CH^3)^2$, is formed by the dry distillation of tetramethyl-diphenylchloroethane (p. 1913); crystallises after some time from the portion of the crude liquid product which boils between 325° and 340° ; and may be purified by draining, pressing, and recrystallisation from alcohol. It forms shining crystalline spangles, melts at 105° – 106° , and volatilises without decomposition. It is moderately soluble in boiling alcohol, somewhat more soluble in ether and in carbon sulphide. When dissolved in either of these last two solvents, it unites directly with bromine, the solution after some time depositing small shining needles, which are but very slightly soluble in ether or in carbon sulphide.

Together with the solid tetramethylstilbene there is formed a somewhat considerable quantity of a liquid isomeric compound boiling at 335° ; it has not, however, been obtained quite free from dissolved stilbene. A solution of bromine in carbon sulphide, even when very dilute, is decolorised by this liquid compound, with evolution of hydrogen bromide, and after filtering from traces of tetramethyl-stilbene bromide, there remains a colourless oil which does not solidify even after prolonged contact with the air.

Xylene prepared from parabromotoluene yields, when treated with dichloroethyl oxide and sulphuric acid, a tetramethyldiphenylchloroethane, from which, by dry distillation, there is obtained a large quantity of a liquid and a small quantity of a solid tetramethylstilbene, the latter, however, being not identical but isomeric with that above described, inasmuch as it crystallises in shining laminae melting at 157° .

Solid tetramethylstilbene (m. p. 105° – 106°), boiled for twenty-four hours with dilute nitric acid (1 vol. HNO^3 of sp. gr. 1.4 and 3 vol. water), yields [1 : 2 : 4] xylic acid (CO^2H in 1), melting at 122° ; consequently tetramethylstilbene from coal-tar oil consists for the most part of the modification in which the CH -groups occupy the position 1, and the methyl-groups the places 2 and 4:



TETRAMORPHINE, $C^{18}H^{12}N^2O^{24}$, is formed by the action of dilute sulphuric acid on morphine, first at 100° , and afterwards at 140° (vii. 821); also by the action of sodium ethylate on a solution of tetracetylmorphine in benzene (Beckett a. Wright, *Chem. Soc. J.* xxviii. 323).

TETRAMAPHTHOL - HEMIANTHYRIDIC - PYROMELLITIC ACID, $C^{20}H^2O^7$. See PYROMELLITIC ACIDS (vii. 840).

TETRANITRO-ANTHRAFLAVONE, $C^{14}H^4(NO^2)^4O^4$, is prepared by heating 5 g. anthraflavone (p. 107) with 150–160 g. nitric acid sp. gr. 1.4 in a reflux apparatus till the whole is dissolved, and separates on cooling and dilution with water in shining yellow needles which melt at 307.5° (corr.) with explosion and combustion. In water, especially when hot, it dissolves readily with yellow colour; in alcohol and ether with red colour; from its yellow alkaline solutions it is precipitated by acids. Strong nitric acid converts tetranitro-anthraflavone into a compound which is not precipitable by water, and crystallises in yellow plates. Tetranitro-anthraflavone sometimes remains unaltered in dry air, sometimes turns red on the surface. It absorbs dry ammonia gas, forming a light red compound, $C^{14}H^2(NO^2)^4(NH^4)^2O^4.2NH^3$, which gives off 1 mol. ammonia over calcium chloride, and 2 mol. when heated. $C^{14}H^2(NO^2)^4(NH^4)^2O^4$ is a dark-red body which dissolves readily in water, the solution when exposed to the air emitting a faint musk-like odour, arising from decomposition of the salt, which takes place with deposition of free tetranitro-anthraflavone. From the aqueous solution of the ammonium salt, silver fluoride or nitrate throws down the compound $C^{14}H^2(NO^2)^4Ag^2O^4$ in slender brownish needles having a silky lustre. With sodium-amalgam, and with tin and hydrochloric acid, tetranitro-anthraflavone yields

ill-defined or easily decomposable compounds. The mother-liquors of the preparation of tetranitro-anthraflavone contain trinitro-hydroxybenzoic acid (F. Schardinger, *Ber.* viii. 1487).

TETRANITRO-AZOKYBENZENE, $C^{12}H^4(NO^2)^4N^2O$, is formed, with energetic action, when diphenylthiocarbamide is added by small portions to fuming nitric acid, and on pouring the solution into water, boiling the resulting precipitate with alcohol, and crystallising the residue from strong nitric acid, the tetranitro-compound separates in yellow crystals (A. Fleischer, *Ber.* ix. 993).

TETRANITRO - BENZYL-TOLUENE, $C^{14}H^{10}(NO^2)^4$. See **TOLUENE** (BENZYL-).

TETRANITROCARBANILIDE, $CO[NH.C^6H^3(NO^2)^2]^2$ (Losanitsch, *Ber.* x. 690; xi. 1539). This compound is formed by the action of nitric acid on thiocarb-anilide or dinitrothiocarb-anilide. It is insoluble in water, slightly soluble in alcohol and ether, and crystallises from solution in hot nitric acid in yellow needles, melting at a temperature above 200° . With alkalis it forms red salts, from which it is precipitated by acids. When drenched and afterwards boiled with alcoholic potash, it yields the potassium salt $CO[NK.C^6H^3(NO^2)^2]^2$, which is red when first prepared, but afterwards turns green, and is converted, by contact with water at ordinary temperatures, into a red compound, at the boiling heat into a yellow precipitate consisting of dinitranilino. The potassium salt is decomposed in a similar manner in alcoholic solution. Acids also act upon it in like manner, but in this case the greater part of the product is reconverted into tetranitrocarbanilide. The potassium salt, when heated, decomposes with explosion, formation of hydrocyanic acid, and separation of carbon. Tetranitrocarbanilide likewise unites with other bases, but the resulting compounds are very unstable, the yellow needles of the calcium salt falling to pieces as soon as they are removed from the mother-liquor, and the red ammonium salt decomposing when its solution is heated. The action of aqueous potash on tetranitrocarbanilide is different from that of alcoholic potash.

Tetranitrocarbanilide may also be conveniently prepared by the action of hot strong nitric acid on diphenyl-guanidine, and on carbanilide; but in this case there is also formed a small quantity of picric acid, together with a yellow body melting at 204° , which is found in the last mother-liquors, crystallises in spherical groups of needles, and appears to be an isomeric of tetranitrocarbanilide.

TETRANITROCHRYSAZIN, $C^{14}H^4(NO^2)^4O^4$. See **CHRYSAZIN**, under **DIOXY-ANTHRAQUINONES** (p. 108).

TETRANITROCHRYSOPHANIC ACID, $C^{15}H^5(NO^2)^2O^4$. This compound, originally obtained from chrysophanic acid, is also formed by heating chrysarobin (p. 462) with nitric acid of sp. gr. 1.4 (Liebermann a. Seidler, *Ber.* xi. 1603).

TETRANITROCORALLINPHTHALEIN, $C^{20}H^{10}(NO^2)^4O^4$. See **CORALLIN-PHTHALEIN**, under **ROSAURIN** (p. 1764).

TETRANITRO- β -DINAPHTHYLTRICHOLOETHANE, $C^{22}H^{10}(NO^2)^4Cl^2$. See **NAPHTHALENE** (p. 1347).

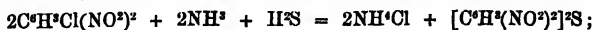
TETRANITRODIPHENYLAMINE, $C^{12}H^7(NO^2)^4N$. See **PHENYLAMINES** (p. 1549).

Tetranitrodibromodiphenylamine, $C^{12}H^8Br^2(NO^2)^4N$, is produced by the action of fuming nitric acid on tribromomethyl-diphenylamine, and crystallises from glacial acetic acid in yellow nacreous laminae or rhombohedral tablets. It does not appear, however, to have been obtained pure, as the product examined turned dingy green on exposure to the air, and varied in melting point between 235° and 242° . It exhibits acid properties (Gnehm, *Ber.* viii. 925).

TETRANITROFLUORESCIN, $C^{20}H^8(NO^2)^4O^4$. See **PHTHALEINS** (p. 1608).

TETRANITRONAPHTHALENE, $C^{10}H^4(NO^2)^4$ (p. 1353).

TETRANITROPHENYL SULPHIDE, $[C^6H^3(NO^2)^2]^2S$, is formed on passing hydrogen sulphide into a warm alcoholic solution of chlorodinitrobenzene [$1 : 2 : 4$, Cl in 1] (p. 183), mixed with a small quantity of strong ammonia :



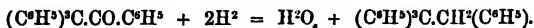
also by treating the same chlorodinitrobenzene with sulphide or hydrosulphide of potassium. It dissolves sparingly in glacial acetic acid, and crystallises therefrom in yellow needles melting at 193° . It is nearly insoluble in benzene, alcohol, and carbon sulphide. Heated at 120° with fuming nitric acid, it is converted into a sulphone,

1916 TETRAPHENYLETHANE—TETRAPHENYLMELAMINE.

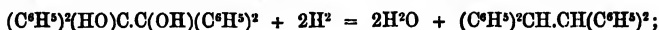
which crystallises from glacial acetic acid in yellow prisms melting at 240°–241° (Beilstein a. Kurbatow, *Ber.* x. 1993).

TETRANITRO-OXYSULPHOBENZIDE, $[\text{C}^6\text{H}^2(\text{NO}_2)^2\text{OH}]^2\text{SO}^2$ (p. 1476).

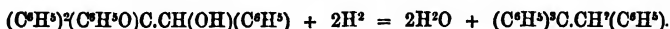
TETRAPHENYLETHANE, $\text{C}^{20}\text{H}^{22} = \text{C}^2\text{H}^2(\text{C}^6\text{H}^5)^4 = (\text{C}^6\text{H}^5)^2\text{HC}.\text{CH}(\text{C}^6\text{H}^5)^2$, or $(\text{C}^6\text{H}^5)^2\text{C}.\text{CH}_2(\text{C}^6\text{H}^5)^2$. This hydrocarbon is formed: 1. From β -benzpinacolin (p. 1629) by the action of hydriodic acid and phosphorus (Thörner a. Zincke, *Ber.* xi. 65):



2. In like manner from benzpinacone (p. 1628) (Graebe, *Ber.* viii. 1054):



or

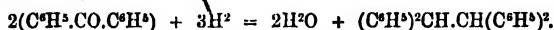


3. By the action of finely divided copper on thiobenzpinacone,



in alcoholic solution (Engler, *Ber.* xi. 922).

4. By heating benzophenone (diphenyl ketone) with zinc-dust (Staedel, *Liebig's Annalen*, cxci. 307):



5. By the action of copper on thiobenzophenone, $\text{C}^6\text{H}^5.\text{CS}.\text{C}^6\text{H}^5$. This method is well adapted for preparing large quantities of tetraphenylethane. The thiobenzophenone is dissolved to saturation in boiling alcohol, and the solution is boiled for several hours in a reflux apparatus with copper precipitated by zinc; or the thiobenzophenone may be mixed with several times its weight of copper, and the mixture distilled from a retort (C. Engler, *Ber.* xi. 926).

6. By the action of sodium on diphenylchloromethane, $\text{CHCl}(\text{C}^6\text{H}^5)^2$, the materials being boiled together in a reflux apparatus for four hours (Engler).

7. By the action of zinc and strong hydrochloric acid on diphenylcarbinol, $\text{C}^6\text{H}^5.\text{CHOH}.\text{C}^6\text{H}^5$, dissolved in glacial acetic acid at the boiling heat (Zagoumeny, *Liebig's Annalen*, clxxiv. 174).

Most of the above reactions are in favour of the symmetrical formula of tetraphenylethane; its formation from β -benzpinacolin, on the other hand, is in favour of the unsymmetrical formula; while the formation from benzpinacone affords no decisive evidence in favour of either formula, since the constitution of benzpinacone itself is still uncertain (p. 1628).

Tetraphenylethane dissolves readily in carbon sulphide and in chloroform, from the latter of which it crystallises remarkably well.

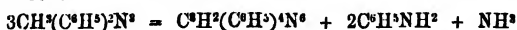
Tetranitrodiphenylethane, $\text{C}^{20}\text{H}^{16}(\text{NO}_2)^4$, is obtained by treating the hydrocarbon with nitric acid at ordinary temperatures; it dissolves in aniline, and separates therefrom in crystals. It is converted by reduction into an amido-compound. **Tetraphenylethane-sulphonic acid**, $\text{C}^{20}\text{H}^{16}(\text{SO}_3\text{H})^4$, is formed from the hydrocarbon by heating with ordinary strong sulphuric acid, and separates from alcoholic solution in crystals. Its **barium salt**, $\text{C}^{20}\text{H}^{16}(\text{SO}_3)^4\text{Ba}^2$, is an easily soluble crystalline mass. The **phenol**, $\text{C}^{20}\text{H}^{16}(\text{OH})^4$, is produced from the sulphonic acid by fusion with potash. When decolorised by animal charcoal, and crystallised from alcohol, to which water is added till the solution becomes turbid, it forms slightly coloured laminae melting at 248° (Lauenstein a. Klotz, *Ber.* xi. 929).

TETRAPHENYLETHYLENE, $\text{C}^{20}\text{H}^{20} = \text{C}^2(\text{C}^6\text{H}^5)^4$. This hydrocarbon, which Behr obtained by the action of finely divided silver on diphenylketonic chloride, $\text{C}^6\text{H}^5.\text{CCl}^2.\text{C}^6\text{H}^5$ (vii. 1150), is also produced by reduction of benzophenone with zinc-dust (Staedel, *Ber.* vi. 178; *Liebig's Annalen*, cxci. 307), and by the action of a strong heat on diphenylmonochlorethane: $2(\text{C}^6\text{H}^5)^2\text{CHCl} = 2\text{HCl} + \text{C}^2(\text{C}^6\text{H}^5)^4$ (Engler a.

Bethge, *Liebig's Annalen*, clxxiv. 194). It melts at 221°. Its **oxide**, $(\text{C}^6\text{H}^5)^2\text{C}=\text{C}(\text{C}^6\text{H}^5)^2\text{O}$, is probably identical with α -benzpinacolin (p. 1629) (Thörner a. Zincke, *Ber.* xi. 1396).

TETRAPHENYLGUANIDINE, $\text{CH}(\text{C}^6\text{H}^5)^4\text{N}^3$. See **GUANIDINE** (p. 908).

TETRAPHENYLMELAMINE, $\text{C}^{27}\text{H}^{22}\text{N}^6 = \text{C}^3\text{H}^2(\text{C}^6\text{H}^5)^4\text{N}^6$ (A. W. Hofmann, *Ber.* vii. 1736). This compound is obtained by heating diphenylguanidine for several hours at 170°–180°:



TETRAPHENYLMETHANE—TETRETHYL-CARBAMIDE. 1917

The hard cake resulting from the reaction is dissolved in alcohol, and the solution is either evaporated or precipitated with water. The body obtained in either way gradually solidifies, but often only after a considerable time; the solidification may, however, be accelerated by heating, solution in alcohol, and reprecipitation with water, or by solution in hydrochloric acid, and precipitation by an alkali; and by repeatedly crystallising the crude crystalline mass from alcohol, the tetraphenylmelamine is obtained in felted needles slightly soluble in ether, insoluble in water, melting at 217° . The hydrochloride of this base forms elongated rhombic prisms; the platinochloride rhombic needles; the nitrate slender needles. Tetraphenylmelamine is not altered by boiling with hydrochloric acid, whereas triphenylmelamine is easily decomposed thereby, taking up water and forming ammonia and phenyl cyanurate.

TETRAPHENYLMETHANE, $C(C^6H^5)^4$, is formed, with evolution of hydrogen chloride, when a mixture of benzene and carbon tetrachloride is heated with aluminium chloride, zinc chloride, or ferric chloride: $4C^6H^6 + CCl_4 = 4HCl + C(C^6H^5)^4$ (Friedel & Craft, *J. pr. Chem.* [2], xvi. 233).

TETRAPHENYLPHOSPHOTRISULPHIDE, $P^4S^3(C^6H^5)^4$, is formed, together with isophosphophenylsulphide (p. 1575), by the action of dry hydrogen sulphide on phosphenyl dichloride (p. 1576).

TETRAPHENYL-TETRAZONE, $(C^6H^5)_4N=N=N-N(C^6H^5)_2$, is formed by oxidation of diphenylhydrazine with mercuric oxide at ordinary temperatures and in dilute solution (see HYDRAZINES, p. 1059).

TETRAPLATINOSULPHOPLATINATE, Pt^4S^6 , and **TETRAPLATINOSULPHOSANNNATE**, Pt^4SnS^6 . See SULPHIDES (pp. 1847, 1848).

TETRAPOTETRAMORPHINE, $C^{186}H^{144}N^8O^{20} = 4C^4H^8N^2O^5 - 4H^2O$, is formed by heating codeine with hydrochloric acid at 100° (vii. 375).

TETRAPROPYLARSONIUM IODIDE, $As(C^3H^7)^4I$. When propyl iodide is heated with arsenic at 175° – 185° for twenty-four to thirty hours, a brown-red liquid is formed, which solidifies in the cold to reddish-brown crystals having the composition $AsI^3, As(C^3H^7)^4I$. This compound is decomposed by boiling concentrated potash-ley, with separation of an oil, and, after the excess of potash has been saturated with carbonic acid, absolute alcohol extracts from the product, tetrapropylarsonium iodide. The solution of this salt dissolves iodine when heated, giving rise to a *periodide*, which separates on cooling in blackish-brown crystals having a metallic lustre. On distilling the compound $AsI^3, As(C^3H^7)^4I$ with potash, *tripropylarsine*, $As(C^3H^7)^3$, passes over as a very fetid liquid, which unites directly with iodides of alcohol-radicles (Cahours, *Compt. rend.* lxxvi. 1383).

TETRAPROPYLPHOSPHONIUM IODIDE, $P(C^3H^7)^4I$. See PHOSPHINES (vii. 955).

TETRATEREBENTHENE, $C^{101}H^{64}$, is formed by the action of antimony trichloride on terebenthene. It is an amorphous brittle solid resembling colophony, of faint yellow colour, almost insoluble in alcohol, soluble in ether, carbon sulphide, petroleum, and turpentine oil, and remains on evaporating the solvent in the form of a yellow varnish. It is dextrogyrate; $\alpha_D = +20^{\circ}$. Sp. gr. at $0^{\circ} = 0.977$. It softens at about 100° , and begins to decompose at an incipient red heat, yielding a terpene, $C^{16}H^{16}$, boiling at 176° , colophene, $C^{20}H^{22}$, and other high-boiling products soluble in alcohol. Pulverised tetraterebenthene absorbs oxygen from the air, especially when heated, but does not produce an acid. It absorbs dry hydrogen chloride, forming $C^{10}H^{64}, 2HCl$, and when hydrogen chloride or bromide is passed into its ethereal solution, the compound $C^{10}H^{64}, 2HCl$ or $C^{10}H^{64}, 2HBr$ is produced. The dihydrochloride remains on evaporating the ether, and heating the residue in a vacuum at 100° , as a brittle easily friable mass (Ribian, *Compt. rend.* lxxix. 389).

TETRATHIONIC ACID, $H^2S^4O^6$. See SULPHUR, ACIDS OF (p. 1882).

TETRATHIOPHOSPHATE, TRIPHENYLIC, $PS(SC^6H^5)^3$. See PHOSPHORIC ETHERS (p. 1603).

TETRATOLYLMELAMINE, $C^8H^2(C^7H^7)^4N^6$, is prepared, like the corresponding phenyl-compound, by the action of heat on ditolylguanidine, and is obtained as a resin which slowly acquires a crystalline structure. Its hydrochloride crystallises in concentric groups of slender needles (Hofmann, *Ber.* vii. 1736).

TETRETHYL-CARBAMIDE, $N(C^2H^5)_2.CO.N(C^2H^5)_2$. See CARBAMIDES (p. 390).

TETRETHYL-DIAMIDOBENZOPHENONE, $\text{CO}[\text{C}^6\text{H}^4\text{N}(\text{C}^2\text{H}_5)^2]^2$. See **KETONES** (p. 1154).

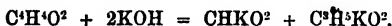
TETRETHYL-TETRAZONE, $(\text{C}^2\text{H}_5)^2\text{N.N}=\text{N.N}(\text{C}^2\text{H}_5)^2$. See **HYDRAZINES** (p. 1062).

TETRIC ACID AND ITS HOMOLOGUES (Demarcay, *Compt. rend.* lxxiii. 449; lxxvi. 1085; lxxvii. 351; lxxviii. 126, 289; *Bull. Soc. Chim.* [2], xxvii. 483; xxxiii. 516, 575; xxxiv. 31; *Chem. Soc. J.* xxxv. 457-460; xxxvii. 625). These acids, represented by the general formula $\text{C}^n\text{H}^{2n-4}\text{O}^2$, are formed by the successive action of bromine and alcoholic potash on the ethylic ethers of aceto-acetic acid and its homologues: see **HEPTIC ACID** (p. 1020). In the free state they have the composition $3\text{C}^n\text{H}^{2n-4}\text{O}^2 + \text{H}^2\text{O}$ or $\text{C}^{3n}\text{H}^{6n-10}\text{O}^7$, and this triple molecule may exist in their salts, barium heptate, for example, having the composition $\text{C}^{21}\text{H}^{30}\text{BaO}^7$; but it is broken up by the more powerful reagents, such as bromine, phosphorus pentachloride, &c.

Tetric acid, $\text{C}^{12}\text{H}^{10}\text{O}^7 = 3\text{C}^4\text{H}^4\text{O}^2 + \text{H}^2\text{O}$, is a colourless body crystallising from its aqueous solution in triclinic prisms. It is sparingly soluble in cold water, readily in hot water and in alcohol, ether, and a hot mixture of chloroform and alcohol, but insoluble in chloroform alone. It melts at 189° , and, like its homologues, gives a violet-red colour with ferric chloride.

On *Heptic*, *Pentic*, and *Hexic acids*, see pp. 1020, 1499, 1501.

These acids are decomposed by strong aqueous potash at 150° , yielding formic acid and a higher acid of the fatty series; tetric acid, for example, yielding formic and propionic acids:



They are said to form remarkable salts, in which the radicle $\text{C}^n\text{H}^n\text{O}^2$, &c., acts like silica, several molecules uniting with one or more molecules of a base. With fuming nitric acid, they yield nitro-derivatives. In sulphuric acid they dissolve without decomposition even at 100° . When treated with chlorine or bromine, they form additive compounds which are not decomposed by water. Nascent hydrogen does not act upon them.

By the action of phosphorus pentachloride on tetric acid, an oily chlorinated product is obtained according to the equation $(3\text{C}^4\text{H}^4\text{O}^2 + \text{H}^2\text{O}) + 4\text{PCl}_5 = 2\text{HCl} + 4\text{PCl}_3\text{O} + 3\text{C}^4\text{H}^4\text{Cl}^2\text{O}$. The oil may be separated from the other products by treatment with water, in which it is insoluble. It has a faint aromatic odour, boils at 171° - 172° with slight decomposition, and has a density of 1.471 at 10° . It unites readily with bromine or chlorine, forming the compounds $\text{C}^4\text{H}^4\text{Cl}^2\text{Br}^2\text{O}$, m. p. 67° - 67.5° , and $\text{C}^4\text{H}^4\text{Cl}^4\text{O}$, m. p. 48° - 48.5° . These are crystalline bodies, which are not decomposed by water, alcohol, ammonia, or potash, and probably consist of chlorobromo- and tetrachloro-ketones. Fuming nitric acid dissolves the compound $\text{C}^4\text{H}^4\text{Cl}^2\text{O}$, forming a nitro-acid. Sulphuric acid dissolves it with purple colour.

The homologues of tetric acid form analogous compounds, resembling $\text{C}^n\text{H}^n\text{Cl}^2\text{O}$ in their chemical and physical properties. $\text{C}^3\text{H}^3\text{Cl}^2\text{O}$ boils at 189° - 192° , decomposing at the same time. Its homologues are not volatile without decomposition.

Hydroxytetric Acid and its Homologues, $3\text{C}^n\text{H}^{2n-4}\text{O}^3 + \text{H}^2\text{O} = \text{C}^{3n}\text{H}^{6n-10}\text{O}^{10}$. These acids, also called *tetrenic*, *pentic acid*, &c., are formed by acting on the ethylic ethers of aceto-acetic acids with 2 mols. bromine, and treating the products with alcoholic potash (pp. 1020, 1499, 1501).

Hydroxytetric acid, $3\text{C}^4\text{H}^4\text{O}^3 + \text{H}^2\text{O}$ (m. p. 203° - 204°), crystallises from boiling water in small rounded masses formed of minute needles. It is very soluble in boiling water, alcohol, and ether, but is insoluble in chloroform, as are also its homologues.

Hydroxypentic acid, $3\text{C}^3\text{H}^3\text{O}^3 + \text{H}^2\text{O}$ (m. p. 193°), behaves with boiling water like the preceding, but is less soluble in cold water, and its crystalline form is different.

Hydroxyhexic acid, $3\text{C}^3\text{H}^3\text{O}^3 + \text{H}^2\text{O}$ (m. p. 173° - 174°), derived from ethylic propyl-acetoacetate, separates from its solution in boiling water in very small needle-shaped plates.

Isohydroxyhexic acid (m. p. 186° - 187°), derived, in like manner, from ethylic isopropylacetoacetate, separates from alcoholic solution in fine monoclinic crystals.

All these acids easily decompose carbonates. Their salts correspond with the formula (for hydroxytetric acid) $3\text{C}^4\text{H}^3\text{MO}^3 + \text{M}^2\text{O}$, and are generally well crystallised. The copper and silver salts are but slightly soluble in water.

The acids are easily converted into ethereal salts by treatment with alcohol at 150° . Nascent hydrogen is fixed by them thus: $(3\text{C}^4\text{H}^4\text{O}^3 + 3\text{H}^2\text{O}) + 3\text{H}^2 = 3\text{C}^4\text{H}^4\text{O}^2 + 3\text{H}^2\text{O}$. The *hydro-hydroxytetric acid* thus obtained (m. p. 111°), crystallises easily in indistinct masses, and is very soluble in water, alcohol, and ether. Its homologues

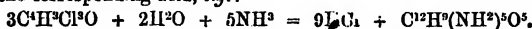
are less and less soluble in cold water. These bodies on treatment with alcohol at 150° are converted into ethereal salts having a faint and agreeable odour.

Phosphorus pentachloride acts on hydroxytetric acid and its homologues, in the manner shown by the equation $(C^4H^4O^3 + H^2O) + 7PCl^5 = 7POCl^3 + 5HCl + 3C^4H^4Cl^3O$.

The chlorinated oils from the higher homologues are attacked by water with difficulty, but hydroxytetric chloride is easily attacked by cold water. These chlorides cannot be distilled at the ordinary pressure without decomposition. They react with alcohol in two stages, the first being represented by $C^4H^4Cl^3O + 2C^2H^4O = 2HCl + C^4H^4ClO(OC^2H^3)^2$. This reaction takes place on dissolving the chloride in a large excess of cold alcohol; if ammonia be then added, the following reaction occurs: $C^4H^4ClO(OC^2H^3)^2 + NH^3 = HCl + C^4H^4(NH^2)O(OC^2H^3)^2$. This amidated ethereal salt crystallises easily in large satiny needles, slightly soluble in cold water.

The second stage of the action of alcohol on these chlorides is represented by the equation $C^4H^4ClO(OC^2H^3)^2 + HOC^2H^3 = C^4H^4O(OC^2H^3)^3 + HCl$; and if the alcohol contains water, the following reaction also occurs: $C^4H^4OCl(OC^2H^3)^2 + H^2O = C^4H^4O(HO)(OC^2H^3)^2 + HCl$. This last ethereal salt is also produced in a state of purity by prolonged boiling of the amidated ethereal salt with water.

These ethers, when treated with aqueous ammonia, ultimately yield an amide, which is also obtained as the final product of the action of aqueous ammonia on the chloride of the corresponding acid, e.g.:



The body $C^{12}H^9(NH^2)^5O^5$ thus produced is the true amide of hydroxytetric acid.

TEUCRIN, $C^{12}H^{20}O^{11}$. A glucoside obtained from *Teucrium fruticans*, a Sicilian plant used as a remedy for intermittent fever. Nitric acid converts it into a crystallised acid having the composition $C^8H^8O^3$ (Ogialoro, *Gazz. chim. ital.* viii. 440).

THALLENE. A solid hydrocarbon, isomeric with anthracene, obtained from the last products which pass over in the distillation of American petroleum. It is distinguished by a splendid green fluorescence, and when illuminated by violet and ultra-violet light, exhibits a fluorescence-spectrum containing light green bands (H. Morton, *Chem. News*, xxvi. 199, 272; xxxiv. 18; *Phil. Mag.* [4], xvi. 89; *Chem. Soc. J.* xvi. 235; xxvii. 14; xxxii. 422; *Jahresb. f. Chem.* 1872, 150; 1873, 158).

THALLIUM. Atomic Weight 203.642 (Crookes).

Occurrence.—Thallium is found in the form of an alum on the island of Vulcano (see MINERALS, p. 1331).

Preparation.—A method of separating thallium from the flue-dust of pyrites-burners, depending on the formation of thallium-alum, is described by F. Stolba (*Ber. d. Königl. böhm. Gesellsch. d. Wissenschaften*, Nov. 7, 1873). The flue-dust is first separated from extraneous matters by passing it through a coarse sieve, and then boiling it with water acidified with sulphuric acid. The pasty mixture is thrown on a large filter, and after the dropping has ceased, hot water is added with vigorous stirring. The wash-water serves, after acidification, for lixiviating a fresh portion. The first tolerably concentrated filtrate is evaporated to the crystallising point in very shallow basins, when, on cooling, large beautiful roddish crystals of thallium-aluminium-iron alum are formed. The mother-liquors, after addition of aluminium sulphate, and on more evaporation, yield a small quantity of mixed alums. The last mother-liquors, with the washings of the crystals precipitated by crude hydrochloric acid, deposit a very small quantity of thallium chloride. The crude thallium-alum crystals are twice crystallised from an aqueous solution acidified with sulphuric acid, whereby a pure alum is obtained, yielding pure metallic thallium when treated with zinc and dilute sulphuric acid, and pure thallium chloride on treatment with hydrochloric acid. Crude thallium chloride may also be first prepared, converted by sulphuric acid into sulphate, and then by means of aluminium sulphate into thallium alum, which is purified by recrystallisation. The first-named method is, however, the more convenient. The decomposition of the chloride by sulphuric acid being troublesome. The thallium alum is much more readily soluble in hot than in cold water: hence the advantage gained by the conversion of the much less soluble thallious sulphate into the corresponding alum.

Another method of preparation is described by R. Nietzki (*Dingl. pol. J.* cexix. 262). The thallious chloride obtained from the flue-dust by precipitation with hydrochloric acid is mixed with acidulated water, and a few strips of zinc are immersed in the liquid, whereby, in the course of a few days, the entire quantity of thallious chloride is converted into a muddy deposit of metallic thallium, which is then washed and dissolved in dilute sulphuric acid. From this solution, pure thallious sulphate may be obtained by crystallisation, and this salt, when decomposed by the electric current, yields pure thallium.

Heat of Solution of Thallium-compounds.—The following determinations have been made by Thomsen (*J. pr. Chem.* [2], xix. 13):

	Grm. deg.		Grm. deg.
(TlCl, Aq) =	— 10100	Tl ₂ O, Aq =	— 3080
(TlBr, Aq) =	— 13750	Tl ₂ S, Aq =	— 33770
(TlI, Aq) =	— 17850		

Reactions.—1. Thallious chloride is very easily converted into *sulphate* by adding it to fused sodium-hydrogen sulphate, or to a solution of sodium sulphate of 3°–5° B. From the resulting solution, after slight acidulation, the thallium may be precipitated in the metallic state by zinc (Krause, *Dingl. pol. J.* cccvii. 323).

2. When thallic oxide, Tl₂O₃, is mixed with about an eighth of its weight of *stannic sulphide* prepared in the dry way (mosaic gold), a mixture is obtained which, when rubbed with moderate force, or touched by an electric spark, takes fire and burns quickly without detonation (Böttger, *N. Rep. Pharm.* xxiv. 243).

3. According to Schöne (*Bull. Soc. Chim.* [2], xxix. 538), *hydrogen dioxide*, either liquid or gaseous, converts thallious oxide into a brown oxide insoluble in water. Consequently the brown coloration of an ozonoscope impregnated with thallium cannot be regarded as a proof of the presence of ozone, since former experiments of Schöne have shown that hydrogen dioxide is always present in the air.

Blowpipe Reaction.—Thallium salts, fused with borax and phosphorus salt, form colourless glasses, which become gray and opaque when heated for a short time in the reducing flame (E. J. Chapman, *Phil. Mag.* [5], ii. 397).

Estimation.—According to Phipson (*Compt. rend.* lxxviii. 563), thallium cannot be exactly estimated in the form of a thallic compound, but must first be reduced to the thallious form. For this purpose the solution of a thalliferous mineral in aqua regia is treated, after sufficient dilution, with hydrogen sulphide; the filtrate is heated to boiling, as far as possible out of contact with the air, to expel the excess of the reagent; then mixed with a slight excess of sodium carbonate, and quickly filtered; and the filtrate is treated with ammonium sulphide, which precipitates the thallium completely as thallious sulphide.

Nietzki (*Zeitschr. anal. Chem.* 1877, 422) estimates thallium by means of the insolubility of thallious iodide in a concentrated solution of potassium iodide. From dilute solutions the thallium is first precipitated by potassium iodide; the precipitate is collected on a filter, and treated with sulphuric acid till the whole of the iodine is expelled; and the concentrated solution thus obtained is titrated.

On the separation of Thallium from Vanadium, see VANADIUM.

Thallious Chloride, TlCl. Carnelley a. Williams, by the method already described (p. 941), found that this compound boils between 719° and 731°. At a lower temperature it melts to a pale yellow liquid, changing to cherry-red, and finally again to yellow.

The vapour-density was found by Roscoe (*Proc. Roy. Soc.* xxvii. 426) to be between 7.4 and 8.75, the calculated value for TlCl being 8.49.

Iodides. *Thallious Iodide*, TlI, boils, with slight decomposition, at 806°–814° (Carnelley a. Williams).

The following observations on the iodides of thallium have been made by Th. Knösel (*Ber.* vii. 576, 893). When yellow thallious iodide (v. 751), precipitated from a hot solution, is suspended in the liquid and exposed to direct sunshine, it turns green without change of composition, the yellow colour being, however, restored by various reagents, e.g. iodine-water or potassium iodide. The dry green substance, when heated, first turns yellow, then at a higher temperature orange-red, and by fusion and sublimation red transparent granules are obtained, which after some time become yellow. By contact with iodine, the green compound is converted into a black iodide containing, according to Knösel's analysis, 51.455 per cent. thallium, whence he deduces the formula Tl²I³. This, however, requires 51.71 per cent. thallium, and the experimental number agrees much better with Jørgensen's *thallosothalline iodide*, Tl²I⁴ (v. 1151), which requires 54.6 per cent.

Thallium Cyanides. See CYANIDES (p. 611); on Thallious Platinocyanide, p. 616.

Thallium-ethyl Sulphide, or **Thallium Mercaptide**, Tl.S.C²H⁵, is formed on agitating a solution of thallium carbonate with mercaptan, as a yellow curdy precipitate which dissolves in water with alkaline reaction, oxidises on exposure to the air, slowly at ordinary temperatures, more quickly when heated, and is decomposed by acids, with evolution of mercaptan (Claesson, *J. pr. Chem.* [2], xv. 193).

Thallium-diethyl Compounds (F. C. Hartwig, *Ber.* vii. 298; *Liebig's An-*

nales, clxxvi. 257). The *chloride*, $\text{Th}(\text{C}^2\text{H}^3)^2\text{Cl}$, is produced when an ethereal solution of thallium trichloride, prepared by the action of chlorine on thallious chloride suspended in pure and dry ether, and freed by carbon dioxide from chlorine, hydrogen chloride, and the products of the action of chlorine on ether—is slowly added to zinc-ethyl mixed with twice its volume of ether; and by washing the product with water and crystallising it from boiling water, the pure chloride is obtained in beautiful shining scales. It is somewhat altered by exposure to light, and decomposes with slight detonation when heated to 190° , yielding thallious chloride and a combustible gas. The estimation of the thallium in this compound is best effected by mixing it in a beaker with nitric acid, neutralising with sodium carbonate, precipitating the concentrated solution with potassium iodide, washing the precipitated thallium iodide, and drying it at 100° .

The following salts were obtained by double decomposition between the chloride of thallium-diethyl in aqueous solution and the corresponding silver salts, except the iodide, which was prepared by mixing solutions of thallium-diethyl sulphate and barium iodide, the thallium-diethyl iodide being then extracted from the precipitate with boiling water.

The *sulphate*, $[\text{Th}(\text{C}^2\text{H}^3)^2]^2\text{SO}_4$, forms needles grouped in stars, is very soluble, and explodes at 205° . The *phosphate*, $[\text{Th}(\text{C}^2\text{H}^3)^2]^2\text{PO}_4$, forms needles which explode at 189° , and are easily soluble in water or alcohol, but less soluble in hot than in cold water. The *nitrate*, $\text{Th}(\text{C}^2\text{H}^3)^2\text{NO}_3$, dissolves with difficulty, and explodes at 236° . The *acetate*, $\text{Th}(\text{C}^2\text{H}^3)^2\text{C}^2\text{H}_3\text{O}_2$, is easily soluble in water or alcohol, and crystallises in hard, slender needles, melting at 212° , and distilling almost without decomposition at 245° ; when it explodes if rapidly heated. The *iodide*, $\text{Th}(\text{C}^2\text{H}^3)^2\text{I}$, forms white, silky leaflets, which explode at 195° , and dissolve in 1,000 pts. of cold water.

The *hydrate of thallium-diethyl* was obtained in silky needles, by precipitating a solution of the sulphate with barium hydrate, and evaporating the filtrate. It explodes if rapidly heated to 211° , and dissolves more readily in cold than in hot water. The solution is alkaline, and on neutralisation with acids yields the salts already described; it does not, however, unite with carbonic acid.

Thallium-triethyl does not appear to be produced by the action of thallium trichloride on zinc-ethyl, even when an excess of the latter is employed, and the action of zinc-ethyl on thallium-diethyl chloride yields not thallium-triethyl, but metallic thallium, zinc chloride, and a gas, which is probably a mixture of ethylene and ethane. The iodide of thallium-diethyl reacts in a similar manner.

Thallium-salicylanilide, $\text{C}^6\text{H}^4(\text{OTl})\text{CO}\cdot\text{NH}\cdot\text{C}^6\text{H}^5$, formed by heating thallious hydrate with salicylanide, crystallises in faintly-yellowish shining laminae, sparingly soluble in water, more freely in alcohol, nearly insoluble in ether (Kupferberg, *J. pr. Chem.* [2], xvi. 424).

THAPSIA. The root-bark of *Thapsia garganica* and *Th. Silivum* has been analysed by Yvon (*Pharm. J. Trans.* [3], viii. 162), who found in the dry bark:

	Th. gargan.	Th. Silivum
Starch	22.510	26.124
Gum	5.179	5.421
Gum-resin	5.759	4.271
Resin	2.554	3.192
Albumin	1.354	0.624
Chalk	1.365	1.368
Magnesia	0.677	0.697
Iron	0.370	0.224
Alumina	0.338	0.508
Sulphuric acid	0.297	0.300
Phosphoric acid	1.468	1.919
Chlorine	0.219	0.420
Silica	2.715	0.707
	44.805	45.775

THAUMASITE. A mineral from the Areskutan mountain in Sweden, having, according to an analysis by G. Lindström, the composition $\text{CaSiO}_3, \text{CaSO}_4, \text{CaSO}_4, 14\text{H}_2\text{O}$ (A. E. Nordenskiöld, *Compt. rend.* lxxxvii. 313).

THEBAINE. This alkaloid, treated with excess of *acetic anhydride*, yields an amorphous base, probably a polymerised body, which dissolves in ether, and forms an amorphous hydrochloride and platinochloride (Beckett a. Wright, *Chem. Soc. J.* xxix. 652).

Thebaine, treated with *sulphuric* and *iodic acids*, assumes a violet colour, which

however disappears on addition of sodium carbonate (Selmi, *Monit. Scientif.* 1878, 692).

On the Detection and Estimation of Thebaine in mixtures of Alkaloids, see PLANT-BASES (p. 1635).

THEOBROMIC ACID, $C^8H^{12}O^2$. This acid, the highest known member of the fatty series, has been obtained by Kingzett (*Chem. Soc. J.* xxxiii. 38) from cacao-butter by saponification and fractional crystallisation of the product. It melts at 72.2° , distils without decomposition at a higher temperature, and becomes electric by friction, a property likewise exhibited by its silver salt. Together with this acid there is obtained another fatty acid, having the composition of lauric acid, $C^{12}H^{24}O^2$; but it melts at 57.5° , whereas lauric acid melts at 43° : hence it is probably a mixture of an acid lower in the series than lauric acid with another of higher melting point than the latter.

THEOBROMINE, $C^7H^8N^4O^2$. For the separation of theobromine from cacao, G. Wolfram (*Dingl. pol. J.* cccxxx. 240; *Chem. Soc. J.* xxxvi. 406) recommends the use of sodium phosphotungstate. The aqueous infusion of the cacao is precipitated with a lead salt; the precipitate, after removal of the lead by hydrogen sulphide, is mixed with sodium phosphotungstate, and this last precipitate is mixed with baryta. According to Trojanowsky (*Dingl. pol. J.* cccxiii. 650), the proportion of theobromine in cacao varies from 1.2 to 4.6 per cent.

On the Detection and Estimation of Theobromine in mixtures of Alkaloids, see PLANT-BASES (p. 1635).

THERMODYNAMICS. When heat is given to or taken from a body, there is caused in general a change of the temperature and volume of the body, and of the stress produced by it on the bodies with which it is in contact: in what follows, unless in special cases, this stress will be taken to be due to a uniform pressure over the whole of the bounding surface. The relation between the simultaneous changes in the three conditions mentioned can be expressed by help of three coefficients—namely, (i) The coefficient of expansion under constant pressure; (ii) The coefficient of increase of pressure at constant volume; (iii) The coefficient of volume-elasticity at constant temperature. These coefficients are defined as follows:

(i). Let v be the volume of unit-mass of substance at temperature t , and dv the increment of volume which takes place when the temperature is raised from t to $t + dt$, the pressure remaining constant; then the coefficient of expansion under constant pressure is:

$$\alpha = \frac{1}{v} \cdot \frac{dv}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ii). Similarly, let p be the pressure per unit of surface of the body at temperature t , and $p + dp$ the pressure per unit of surface when the temperature is $t + dt$, the volume remaining constant, then the coefficient of increase of pressure at constant volume is:

$$\beta = \frac{1}{p} \cdot \frac{dp}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(iii). If the volume diminishes from v to $v - dv$ when the pressure per unit of surface increases from p to $p + dp$, the temperature remaining constant, the coefficient of volume-elasticity at constant temperature is:

$$\epsilon = -v \frac{dp}{dv} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

According to (1) the change of temperature accompanying an infinitesimal change of volume dv at constant pressure is $\frac{1}{\alpha} \frac{dv}{v}$; according to (2) the change of temperature accompanying an infinitesimal change of pressure dp at constant volume is $\frac{1}{\beta} \frac{dp}{p}$. Consequently, if both volume and pressure undergo infinitesimal changes without any alteration of temperature taking place at the same time, the alteration of temperature which would have resulted had volume only been changed must be equal and opposite to that which would have resulted from change of pressure only; that is, if the change is 'isothermal,'

$$\frac{dv}{\alpha v} + \frac{dp}{\beta p} = 0;$$

whence, by (3),

$$\beta = -\frac{\alpha v}{p} \cdot \frac{dp}{dv} = \frac{\alpha \epsilon}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The relation expressed by equation (4) is of importance, since the coefficient β is not accessible to direct experiment, except in the case of gases, whereas α and ϵ can both be found experimentally for solids, liquids, or gases.

In order to express the connection between the quantity of heat lost or gained by a body during given changes of its temperature, volume, and pressure, certain additional coefficients are required, which, to distinguish them from the three above defined, may be called calorimetrical coefficients. A change of temperature is in general determined when the simultaneous changes of volume and pressure are given; similarly, a change of volume is determined by the simultaneous changes of temperature and pressure, or a change of pressure by the simultaneous changes of temperature and volume. Hence a given alteration in the state of a body may be specified in terms of changes in any two of the three conditions in question. Thus, if an infinitely small quantity of heat dQ is imparted to unit-mass of a body occupying the volume v at temperature t and under pressure p , we may, by the use of appropriate coefficients, express the result either as a change of temperature and volume, as a change of temperature and pressure, or as a change of volume and pressure, as follows:

$$dQ = c dt + l dv \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

$$= C dt + h dp \quad . \quad . \quad . \quad . \quad . \quad (5b)$$

$$= \kappa dp + \lambda dv \quad . \quad . \quad . \quad . \quad . \quad (5c)$$

Of the six coefficients here introduced, two, namely, c and C , are well known, the former under the name of the *specific heat at constant volume*, and the latter as the *specific heat under constant pressure*; l is sometimes called the *latent heat of expansion at constant temperature*. In like manner λ might be called the *heat of expansion under constant pressure*, h the *latent heat of increase of pressure at constant temperature*, and κ the *heat of increase of pressure at constant volume*. It is to be noted that all these coefficients are mathematically of the nature of partial differential coefficients. They are not really independent magnitudes, but, as will be shown further on, the six calorimetric coefficients defined by equations (5), together with the three previously defined, may be reduced to *three*, and can thus be expressed in terms of α , ϵ , and \bar{C} , the only ones which have hitherto been determined by direct experiment.

The science of Thermodynamics has reference, in the first place, to the mutual relations and reciprocal transformations of mechanical energy and heat, or thermal energy. But, since energy of every kind can be expressed in terms of mechanical energy, the conclusions of thermodynamics in the widest sense are applicable to electricity and other branches of physics which have not yet received a purely dynamical interpretation. Many results of the greatest scientific importance have indeed been arrived at by this extended application of thermodynamical principles, but in this article it is not proposed to discuss the relations between heat and any other form of energy than the mechanical. This restriction is to be borne in mind in considering some of the general statements that follow, which, if taken in the widest sense, would not be true without qualification.

In numerical statements as to quantities of work and energy, we shall adopt the system of absolute units based on the employment of the *Centimeter, Gram, and Second* as units of length, mass, and time respectively—the system known as the C.G.S. system. In accordance with this, the unit of *force* is the force which, by acting for a second upon one gram, can change its velocity by one centimeter per second. This force is called a *dynes*. The force with which a gram at the sea-level is urged towards the centre of the earth by the resultant effect of the earth's attraction and the centrifugal force due to the earth's diurnal rotation—in other words, the *weight* of a gram,—varies from 978.1 dynes at the equator to 983.1 dynes at the poles. One million dynes, called a *megadyne*, is roughly 2 per cent. more than the weight of a kilogram. The unit of *work*, founded upon the same fundamental units, is the work done when a force of one dyne acts through a distance of one centimeter. This amount of work is called an *erg*. One million ergs—otherwise a *megalerg* or *megerg*—is about 2 per cent. more than 1 kilogram-centimeter; 1 kilogram-meter is about 2 per cent. less than 1000 megalergs. The *energy* of any body or system of bodies is estimated numerically by the amount of work done *by* the body or system of bodies when the energy is expended, or that must have been done *upon* the body (or bodies) to impart to it the energy actually possessed by it. The *erg* is thus the unit for energy as well as for work. Accordingly, the systematic unit for the numerical expression of quantities of heat is the quantity capable of generating an erg, or which is produced by the expenditure of an erg; but, as the statement of quantities of heat in terms of this unit implies a knowledge of the so-called Mechanical Equivalent of Heat, we shall usually express quantities of heat by reference to the amount of heat needed to raise the temperature of 1 gram of water by 1 degree centigrade, and shall call this quantity 1 *gram-degree* of heat. Since, however, the specific heat of water is not constant, a

gram-degree is not a perfectly definite quantity of heat except at an assigned temperature. When the term is used without qualification, it may be taken to mean the quantity of heat needed to raise the temperature of a gram of water from 0°C . to 1°C .

The science of Thermodynamics is based upon two experimentally ascertained principles. The first of these may be stated in the following form:—

I. When mechanical work is done or mechanical energy is expended without producing mechanical energy numerically equal to itself, there is generated a quantity of heat which is proportional to the difference between the quantity of work done, or of energy expended, and the mechanical energy produced; and, conversely, when mechanical energy is produced or mechanical work is done without the expenditure of an equivalent amount of mechanical energy, a quantity of heat disappears which is proportional to the difference between the energy produced, or work done, and the energy expended. Moreover, in both cases the ratio of proportionality is the same; that is to say, the number expressing the ratio between the excess of mechanical energy expended over mechanical energy produced and the quantity of heat generated, in the one case, is the same as that which expresses the ratio of the excess of energy produced over the energy expended to the quantity of heat which disappears in the other case.

An example or two may make the exact meaning of the above statement more evident. Thus, if a body of mass m descends through a height h , the earth exerts upon it a vertical force, $=mg$, during the descent (if g stands for the intensity of gravity), and consequently a quantity of work, $=mgh$, is done upon the body. If the descent takes place by the body falling freely in a vacuum, it receives an increment of kinetic energy, $=\frac{1}{2}mv^2$ (where v^2 is the change in the square of its velocity), such that

$$\frac{1}{2}mv^2 = mgh.$$

In such a case, then, mechanical energy is produced, which is numerically equal to the work done in producing it, and accordingly there is no loss or gain of heat. If, however, the descent of the body, instead of being free, were impeded by friction—as, for example, when a stone slides down a rough plank—the body would not receive so great an increment of velocity as before, and hence its gain of energy would not be equal to the work done. Accordingly a quantity of heat, Q , would be generated, such that

$$JQ = mgh - \frac{1}{2}mv^2,$$

where v^2 is again the change in the square of the body's velocity, and J a numerical factor. Again, if a body is thrown upwards in a vacuum with velocity v , it rises to a height $h = \frac{v^2}{2g}$, and thus gains a quantity of potential energy, mgh , which is numerically equal to the kinetic energy, $\frac{1}{2}mv^2$, which it loses, and in this case no heat appears or disappears. But if a body is started with initial velocity v_1 along a rough level surface, it will, if no work is done upon it, lose kinetic energy without gaining potential energy; or, if work is done on the body so as to keep its velocity constant, there will be expenditure of work without gain of either kinetic or potential energy: in either case a quantity of heat is produced proportional to the loss of energy, or to the expenditure of work, respectively.

On the other hand, a steam-engine can do work, or produce mechanical energy, without any corresponding expenditure of mechanical energy, but while it is doing work a quantity of heat disappears which is in exact proportion to the work done or energy produced.

The facts that the destruction of a given quantity of mechanical energy involves the production of a definite quantity of heat, and that this same quantity of heat disappears when the same given quantity of mechanical energy is generated, is commonly expressed by saying that heat and mechanical energy are mutually convertible. When mechanical energy is destroyed, the number which expresses the ratio of the quantity destroyed to the quantity of heat that appears in its place, or, when mechanical energy is generated, the number expressing the ratio of the quantity generated to the quantity of heat that disappears, is called the **MECHANICAL EQUIVALENT OF HEAT**. This number naturally has different values according to the different units adopted for expressing quantities of mechanical energy or of heat, but the ratio represented by it is essentially constant.

II. The second fundamental principle of Thermodynamics has reference to the conditions which determine how much of a given quantity of heat can be converted into mechanical energy. In various ways it is possible for a body or system of bodies to go through a series of changes of pressure, volume, and temperature, being at the

end of the series in exactly the same condition in all these respects as it was in at the beginning, but so that, during the process, more work is done by the body or system against external forces than is done by external forces upon it. Work is done *by* the body or system when it undergoes a change of size or shape in opposition to external forces; and work is done *upon* the body or system when its size or shape is altered by yielding to external forces. But, since at the end of the process the volume and shape of the body are the same as at the beginning, it follows that the total distance through which the body has yielded to external forces is equal to the total distance through which it has overcome them. Consequently, for the work done by the body to exceed that done upon it, it follows further that the external forces overcome by the body must exceed those to which it yields. This is the same thing as the following shorter but more technical statement: *The stress during decrease of strain must be greater than the stress during increase of strain.* This implies that increase and decrease of strain take place at different temperatures, for the only known way of causing the stress of a body to change while the strain remains constant is to change its temperature; and, in order that this may be, heat must be supplied to the body during part of the series of processes gone through by it, and heat must be withdrawn during another part. If, as generally happens, increase of temperature causes increase of stress with constant strain—for example, increase of pressure with constant volume—heat must be supplied while strain diminishes—that is, while the body does work by changing size or shape in opposition to external forces; and heat must be withdrawn while strain increases—that is, while external forces do work upon the body by altering its size or shape. But if, as happens with water below 4°C. , or with a mixture of ice and water, increase of temperature under constant strain causes decrease of stress, heat must be supplied during increase of strain and withdrawn during decrease of strain. In either case heat must be supplied while the temperature of the body is relatively high, and must be withdrawn while the temperature is relatively low. Moreover, the quantity of heat supplied must be greater than the quantity withdrawn, for, since during the whole series of processes the work done by the body exceeds the work done upon it, and since the final condition of the body is the same in all respects as its initial condition, a quantity of heat proportional to the excess of the former quantity of work over the latter must, in accordance with the First Principle of Thermodynamics, disappear. Now, the Second Fundamental Principle of Thermodynamics asserts that the greatest possible proportion which the quantity of heat so disappearing and converted into work can bear to the total quantity of heat supplied, depends only on the temperatures at which the supply and withdrawal of heat respectively take place, and is quite independent of the nature of the substance or substances which undergo the series of changes supposed.

This result is often referred to as 'Carnot's Principle,' it having been pointed out for the first time by Sadi Carnot (*Réflexions sur la puissance motrice de feu*, 1824), in a form which is substantially the same as that in which it is given above, though the mode of expression was adapted to the hypothesis of the indestructibility of heat.

In this article we have to point out some of the most important verifications which these two fundamental principles have received, and some of the chief results which have been deduced from them.

PRINCIPLE OF THE MUTUAL CONVERTIBILITY OF HEAT AND WORK.

Mechanical Equivalent of Heat.—For general evidence that heat and work are mutually convertible one into the other according to a constant numerical ratio, we may refer the reader to the article HEAT (iii. 125–129, and vi. 685–687 of this work). It may suffice in this place to give the results of two very important redeterminations of the value of this ratio which have been recently carried out.

The first of these redeterminations was made by Joule (*Phil. Trans.* 1878, 365–383; also abstract, stating final result, *Proc. Roy. Soc.* xxvii. 38), by a method essentially similar to that employed by him in 1850 in the experiments referred to in iii. 125–129. The measurement of the work expended was however effected by counting the number of turns of the paddle-wheel and at the same time observing the moment of the couple required to prevent the calorimeter from being carried round with it. This mode of measuring work is similar to that employed by Hirn in his determination of the mechanical equivalent of heat by the friction of water already referred to in vi. 685. Joule states his results in terms of the pound-degree, measured by the mercurial Fahrenheit thermometer, as unit of heat, and the foot-pound at 120 feet above sea-level, in latitude $53^{\circ} 28\frac{1}{2}'\text{N.}$ (at Higher Broughton, Manchester), as unit of work. In five series of experiments he obtained the numbers given in the following table:

Mean temperature of calorimeter (Fahr.) .	58°·5	54°·8	60°·0	58°·1	63°·1
Mean rise of " " " " .	3°·54	3°·77	3°·46	1°·11	5°·22
Mechanical equivalent	772·7	774·6	773·1	767·0	774·0

Taking these numbers as they stand, the mean result is 772·28 foot-pounds at Higher Broughton as the mechanical equivalent of 1 pound-degree at 58°·9 Fahrenheit. But, from circumstances connected with the separate series of experiments, Dr. Joule does not consider them as being all equally trustworthy. Giving to the separate results the relative weights which he assigns to them, the final result may be stated as follows: To raise the temperature of 1 pound of water weighed *in vacuo* from 61·19° to 62·19° of the mercurial Fahrenheit thermometer requires the expenditure of

772·53 foot-pounds

of work at Higher Broughton.

For the sea-level at the latitude of Greenwich, Dr. Joule himself gives as the final result of his experiments

772·55 foot-pounds,

this being the quantity of work required to raise the temperature of a pound of water, weighed *in vacuo*, from 60° to 61° F.

Since the publication of this result, Joule has compared the mercurial-thermometer used in his measurements with one the value of whose readings had been ascertained, in terms of the perfect air-thermometer, by Professor H. A. Rowland, of Baltimore. Applying the corrections calculated by Rowland for the difference between Joule's thermometer and the perfect air-thermometer, we must add 2·94 foot-pounds to the mean as given above, thus getting

775·47

as the corrected value for Manchester. To translate this number from Fahrenheit to Centigrade degrees, and from foot-pounds per pound-degree to centimeter-grams per gram-degree, we must multiply by $1·8 \times 30·48$, which gives

42545·4.

Lastly, to reduce the result to ergs, we must multiply by 981·32, the intensity of gravity in latitude 53° 58½' at 120 feet above sea-level. We thus get, for the absolute mechanical equivalent of a water-gram-degree at mean temperature 16·5° C. :

$4·175 \times 10^7$ ergs.

A second very remarkable series of experiments on the value of the mechanical equivalent of heat has been made by Professor Rowland (*Proceed. Amer. Acad. Arts and Sciences*, xv. [N. S. vii.], 75-200). His method was identical in principle with that employed by Joule, but by modifications in detail he was able to generate heat at a much more rapid rate, thus rendering the corrections for radiation and conduction less important, and to obtain much greater changes in the temperature of his calorimeter—in some experiments as much as 25° or 30° centigrade. His results are all reduced by him to degrees of the perfect air-thermometer, and they lead to the important conclusion that the specific heat of water decreases from temperatures near 0° C. to about 30° and then increases again. The following table gives his results for every fifth degree from 5° to 40° :

Temperature of water	Mechanical equivalent of 1 gram-degree in 10^7 ergs	Temperature of water	Mechanical equivalent of 1 gram-degree in 10^7 ergs
5° C.	4·212	25° C.	4·173
10	4·200	30	4·171
15	4·189	35	4·173
20	4·179	40	4·175

Application to Gases.—It is known experimentally in the case of the more difficultly condensable gases, that (1) at a constant temperature the product of pressure into volume is nearly constant; (2) for a given change of temperature, the ratio in which volume changes when pressure is kept constant is nearly the same as the ratio in which pressure changes when volume is constant, and that this ratio is nearly the same for all gases; (3) the specific heat under constant pressure is nearly independent of pressure or temperature; (4) no appreciable fall of temperature takes place when a gas expands into a vacuum without receiving heat—that is, no appreciable quantity

of work is done in separating the particles of a gas from each other. An ideal substance possessing in perfection the properties here enumerated as belonging approximately to actual gases is called a *perfect gas*. The discussion of the laws of a perfect gas as thus defined is useful as leading to results which are applicable with approximate accuracy to several known gases under ordinary conditions.

Values of the Thermal Coefficients for Perfect Gases.—The properties of a perfect gas in relation to pressure, temperature, and volume, are expressed by the equation

$$p v = R(a + t) \quad (6)$$

where v is the volume occupied by unit-mass of the gas under pressure p and at temperature t , R is a constant depending on the kind of gas, and a a constant depending on the position of the zero and the size of the degrees of the thermometric scale on which the temperature t is expressed. Since the expression $a + t$ occurs very often, it will be convenient to denote it by a single symbol T , writing (6) thus $p v = R T$. Differentiating we get

$$p dv + v dp = R dt \quad (7)$$

which, for the several cases in which dv , dp , or dt respectively = 0, gives

$$\frac{dp}{dt} = \frac{R}{v}, \quad \frac{dv}{dt} = \frac{R}{p}, \quad \frac{dp}{dv} = -\frac{p}{v}.$$

Substituting these values in equations (1), (2), and (3), whereby the coefficients α , β , and ϵ are defined, we get

$$\alpha = \frac{R}{pv} = \frac{1}{a + t}, \quad \beta = \frac{R}{pv} = \frac{1}{a + t}, \quad \epsilon = p.$$

Hence, for all perfect gases, we have

$$\alpha = \beta = \frac{1}{T}.$$

Again, if we equate the values of dQ given in (5a) and (5b), and make $dp = 0$,

$$l = (C - c) \frac{dt}{dv} = (C - c) \frac{p}{R}; \quad (8)$$

or, making $dv = 0$,

$$h = - (C - c) \frac{dt}{dp} = - (C - c) \frac{v}{R}. \quad (9)$$

In like manner, (5b) and (5c) give, for $dp = 0$,

$$\lambda = C \frac{dt}{dv} = C \frac{p}{R} \quad (10)$$

and (5a) and (5c), when $dv = 0$, give

$$\kappa = c \frac{dt}{dp} = c \frac{v}{R} \quad (11)$$

The six calorimetric coefficients are thus reduced, in the case of perfect gases, to the two specific heats C and c ; the three forms of equation (5) may therefore be rewritten as follows:

$$dQ = c dt + \frac{C - c}{R} p dv \quad (12a)$$

$$= C dt - \frac{C - c}{R} v dp \quad (12b)$$

$$= \frac{c}{R} v dp + \frac{C}{R} p dv \quad (12c)$$

For the case in which there is no change of temperature, (12 a) gives

$$dQ = \frac{C - c}{R} p dv.$$

The factor $p dv$ in this last expression represents *work* done during the expansion of the gas against external pressure, and the whole quantity of heat dQ is spent in doing this amount of work, for we have supposed temperature to remain constant, and the substance being a perfect gas, no heat is used up in merely changing its volume. Accordingly, writing dW for $p dv$, we have for the ratio of dW to dQ —the ratio of a quantity of work to the heat expended in doing that work—the

mechanical equivalent of heat. Representing this, as is commonly done, by the symbol J , we get ,

$$J = \frac{dW}{dQ} = \frac{R}{C - c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Equation (13) leads to several noteworthy conclusions. First, it shows that the specific heat at constant volume, c , is constant for the same gas, being independent of volume and temperature, for J , R , and C being all constants, c must be so likewise.

Secondly, the magnitude R , though constant for any one gas, varies for different gases inversely as their densities, so that the product of R for a given gas into the density ρ —or mass of unit-volume under standard pressure and temperature—of that gas, is the same for all perfect gases. Putting $C\rho = \Gamma$, and $c\rho = \gamma$, we have

$$\Gamma - \gamma = \frac{R\rho}{I},$$

where, everything on the right being constant, the left-hand member of the equation is constant also; or, the difference between the thermal capacity under constant pressure and the thermal capacity at constant volume, of so much of any perfect gas as occupies unit of volume under given conditions of pressure and temperature, is independent of the chemical nature of the gas.

Thirdly, since C and the factors which enter into the value of R are all directly measurable by experiment, a knowledge of c , the specific heat at constant volume, for any perfect gas, would enable us to determine the value of J , the mechanical equivalent of heat. We shall see immediately what principles are available for determining the value of c .

Fourthly, by substituting in (8) and (9) respectively the value of $\frac{C - c}{R}$ given by (13), namely, $\frac{1}{T}$, we get the following simple expressions for the coefficients l and h :

$$l = \frac{p}{J} \quad . \quad . \quad . \quad (8') \quad \quad h = -\frac{v}{J} \quad . \quad . \quad . \quad (9')$$

Variation of Pressure, Volume, and Temperature without Gain or Loss of Heat; Adiabatic Changes.—Hitherto we have considered changes of pressure, volume, and temperature as resulting from the addition or removal of heat; but such changes may also take place without any loss or gain of heat. For example, under ordinary circumstances, increase of volume and rise of temperature are observed as the result of heat given to a body, and diminution of volume and fall of temperature as the result of the withdrawal of heat; but, in special cases, a rise of temperature may be exactly compensated by a diminution of volume, or a fall of temperature by an increase of volume, so that, on the whole, there is neither loss nor gain of heat. Changes which take place under such conditions are commonly called *adiabatic changes*, a term introduced by the late Professor Rankine. In general, any change of condition that takes place very rapidly may be considered as being adiabatic, since the quantity of heat that can be lost or gained in an indefinitely short time is itself indefinitely small. From the equations already established, it is easy to deduce expressions which connect the adiabatic changes of volume or of pressure respectively of a perfect gas with the simultaneous changes of temperature, or again which connect adiabatic changes of volume and pressure with each other. This is done by simply putting $dQ=0$ in all the equations; for since dQ represents the quantity of heat lost or gained, the equation $dQ=0$ expresses the condition that any given change is adiabatic.

Equations (12), when $\frac{p}{T}$ is written instead of R , by the characteristic equation of perfect gases (6), become

$$\begin{aligned} dQ &= c dt + (C-c) T \frac{dv}{v}, \\ &= C dt - (C-c) T \frac{dp}{p}, \\ &= \left(\frac{dp}{p} + C \frac{dv}{v} \right) T. \end{aligned}$$

If we combine with these expressions the adiabatic condition $dQ=0$, the first one gives

$$c \frac{dt}{T} + (C-c) \frac{dv}{v} = 0$$

or, if we put k for the ratio of the two specific heats $\frac{C_p}{C_v}$,

$$\frac{dt}{T} + (k-1) \frac{dv}{v} = 0,$$

from which, by integration, we get

$$\left. \begin{aligned} \log_e T + (k-1) \log_e v &= \text{constant} \\ T v^{k-1} &= \text{constant} \end{aligned} \right\} \quad (14)$$

Similarly, the second expression gives

$$\left. \begin{aligned} \log_e T - \frac{k-1}{k} \log_e p &= \text{constant} \\ T p^{\frac{-k-1}{k}} &= \text{constant} \end{aligned} \right\} \quad (15)$$

and the third gives

$$\left. \begin{aligned} \log_e p + k \log_e v &= \text{constant} \\ p v^k &= \text{constant} \end{aligned} \right\} \quad (16)$$

It is easily seen that the three equations, (14), (15), and (16), are not really independent, any one of them following as an immediate consequence from the other two. It may also be noted that any one of them, combined with the equation $p v = R t$, gives the other two.

Work done by the Expansion of a Gas.—If a gas under pressure p undergoes a small increment of volume, dv , it does a quantity of work $dW = p dv$. In general, however, pressure changes at the same time as volume, so that a second increment of volume dv takes place under a different pressure, say p' , the third similar increment under pressure p'' , and so on. Hence the whole amount of work done during a finite change from an initial volume v_0 to the final volume v is

$$W = p dv + p' dv + p'' dv + \dots = \int_{v_0}^v p dv.$$

That is to say, the work done during expansion depends not only on the change of volume and the initial pressure, but on the pressure at each stage of the process. We may consider three special cases:

1. Expansion under constant pressure. In this case we have obviously

$$W = p \int_{v_0}^v dv = p(v - v_0) \quad (17)$$

2. Expansion at constant temperature. In this case we have, by equation (6), $p = \frac{RT}{v}$, and therefore

$$W = RT \int_{v_0}^v \frac{dv}{v} = RT \log_e \frac{v}{v_0}, \text{ or } = RT \log \frac{p_0}{p} \quad (18)$$

3. Expansion without loss or gain of heat. According to (16), when a gas does not lose or gain heat, we have $p = N v^{-k}$, and therefore

$$W = N \int_{v_0}^v v^{-k} dv = \frac{N}{1-k} (v^{1-k} - v_0^{1-k}),$$

or, putting for N its value $p_0 v_0^k$,

$$W = \frac{p_0 v_0}{k-1} \left\{ 1 - \left(\frac{v}{v_0} \right)^{k-1} \right\} \quad (19a)$$

This, on transforming the last term by means of (16) and (14) respectively, gives

$$W = \frac{p_0 v_0}{k-1} \left\{ 1 - \left(\frac{p}{p_0} \right)^{\frac{k-1}{k}} \right\} \quad (19b)$$

and

$$W = \frac{p_0 v_0}{k-1} \left(1 - \frac{T}{T_0} \right) = \frac{R}{k-1} (T_0 - T) = J c (T_0 - T) \quad (19c)$$

Coefficients of Adiabatic and Isothermal Elasticity.—The definition of the coefficient

of volume-elasticity at constant temperature is given by equation (3), namely $\epsilon = -v \frac{dp}{dv}$, and we have already seen that for a perfect gas this becomes $\epsilon = p$. Elasticity of volume being the only kind of elasticity exhibited by gases, we may say generally that the elasticity of a perfect gas at constant temperature is measured by the pressure of the gas. This relation, however, no longer holds good if temperature is not constant. In general, the temperature of a gas varies while it is undergoing any change of volume, and the different ways in which it may vary are infinitely numerous. Hence the coefficient of elasticity of a gas may have an infinite number of different values, and has no definite meaning except under stated conditions. The coefficient corresponding to constant temperature, the value of which has just been given, is often called for distinction the coefficient of *isothermal* elasticity. Another special condition of much importance is that of no loss or gain of heat. The corresponding coefficient of elasticity is called the coefficient of *adiabatic* elasticity, and may be denoted by E . Its value for a perfect gas follows at once from equation (12c), which, with the condition that no heat is lost or gained, becomes

$$c \frac{v}{R} dp + C \frac{P}{R} dv = 0,$$

whence

$$E = -v \frac{dp}{dv} = \frac{C}{c} p. \quad (20)$$

Consequently the adiabatic elasticity of a perfect gas bears to the isothermal elasticity the same ratio as the specific heat under constant pressure bears to the specific heat at constant volume.

Experimental determination of the ratio k of the specific heat C under constant Pressure to the specific heat c at constant Volume.—First Method: A large volume of gas is suddenly compressed, so that its pressure rises from p_1 to p_2 . The process being very rapid, the compression may be considered as taking place without loss or gain of heat; hence, by (15), if the initial temperature be denoted by t_1 , the final temperature t_2 will be given by

$$(a + t_1)p_1^{\frac{1-k}{k}} = (a + t_2)p_2^{\frac{1-k}{k}}.$$

On now leaving the gas to itself without further change of volume, the heat due to the compression will be gradually dissipated, and, when the temperature has returned to the original value t_1 , the pressure will have attained a value, say p_3 , intermediate between p_1 and p_2 . To determine p_3 , we have to consider that p_2 and p_3 are the pressures of the same quantity of gas occupying the same volume at the temperatures t_2 and t_1 ; consequently $\frac{a + t_2}{a + t_1} = \frac{p_2}{p_3}$, and therefore

$$\frac{p_2}{p_3} = \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}}$$

Taking logarithms of both sides, we get from this:

$$\log p_2 - \log p_3 = \frac{k-1}{k} (\log p_2 - \log p_1);$$

whence

$$k = \frac{C}{c} = \frac{\log p_2 - \log p_1}{\log p_3 - \log p_1}. \quad (21)$$

It is evident that a corresponding expression might be obtained as the result of an adiabatic rarefaction instead of an adiabatic compression.

Second Method.—The determination of the ratio $C : c$ by the method last given depends essentially on the relation between simultaneous changes of pressure and temperature during an adiabatic process. Another method may be founded on the relation between changes of pressure and changes of volume during a similar process. The measurement of velocity of sound in air affords the most accurate data for determining this relation, since the alternate compressions and rarefactions which constitute a train of sound-waves follow each other with such rapidity as to be almost strictly adiabatic. From dynamical principles it follows that the velocity with which a disturbance of

the character of a wave of sound is propagated in a medium of density ρ is $V = \sqrt{\frac{E}{\rho}}$

E standing for the adiabatic elasticity as above defined, whose value in the case of a perfect gas is by equation (20), $k p$. This gives for the ratio of the specific heats :

$$k = \frac{C}{\sigma} = V^2 \frac{\rho}{p} \quad (22)$$

Third Method.—Equation (13), namely $R = J(C - c)$, gives an expression for c in terms of C and the mechanical equivalent of heat: $c = C - \frac{R}{J}$. And as both these quantities can be found by direct experiment, the ratio of the two specific heats can be deduced from this expression.

Energy of a Body or System of Bodies.—The principle of the Conservation of Energy may be expressed in relation to the matters under discussion in this article by the equation :

$$J dQ = dI + dW:$$

where $J dQ$ is the energy equivalent to the quantity of heat, dQ , received by a body or system, dI , the increment of energy within the body, and dW the energy given out (whether in the form of heat or of energy in any other form) to other bodies. The terms dI and dW may both be broken up in a manner corresponding to the various effects, internal or external, produced. For the present we will consider internal effects only, and write:

$$dI = J c dt + dM + dK + dP,$$

cdt being the quantity of heat consumed in causing rise of temperature, dM the energy spent in producing molecular changes other than those showing themselves as changes of temperature, dK the increment of the kinetic energy of visible motion, and dP the increment of potential energy (due, for example, to increased height above the sea-level). With this notation we have:

$$JdQ = Jc dt + dM + dK + dP + dW \quad . \quad . \quad . \quad (23)$$

This equation allows us to draw some important conclusions with regard to the flow of fluids. At present we will apply it to the case of a gas forced, at constant pressure p_0 , through a narrow channel or porous plug, on the farther side of which there is a constant pressure p , without loss or gain of heat from external bodies, and without change of level or alteration of potential energy from any other cause. Then $dQ=0$, and $dP=0$; hence, if K_0 , M_0 , W_0 , and t_0 denote initial conditions, and K , M , W , and t the corresponding conditions of the gas after escaping, we have

$$K - K_0 + M - M_0 + W - W_0 + \int_{t_0}^t J/c \, dt = 0.$$

For $K - K_0$ we may write $\frac{1}{2}(u^2 - u_0^2)$, and for $W - W_0$ we may put $p v - p_0 v_0$, where p_0 and p are the pressures on the two sides of the plug, and v_0 and v the corresponding volumes of the unit-mass. Therefore, since for gases c is constant, see (13), and $M - M_1 = 0$:

$$\frac{1}{2}(u^2 - u_0^2) = p_0 v_0 - p v + J c(t_0 - t).$$

Since $p v = R(a + t)$, and $R = J(C - c)$, this gives, if we put $u_0 = 0$:

$$\frac{1}{2}u^2 = J C (t_0 - t) . \quad (24)$$

to determine the velocity u with which a gas escapes from under pressure. To determine $t_0 - t$ in terms of the initial and final pressures, we have, by (15),

$$\frac{a+t_0}{a+t} = \left(\frac{p_0}{p}\right)^{\frac{k-1}{k}}, \text{ and therefore,}$$

$$\frac{1}{2}w^2 = J C (a + t_0) \left[1 - \left(\frac{p}{p_0} \right)^{\frac{k-1}{k}} \right] \quad . \quad . \quad . \quad (25)$$

If the friction of the gas against the channel by which it escapes is so great as to make the final velocity $u=0$, or if the velocity is destroyed by eddies, as happens in any case after a short time, we see by equation (24) that, for a perfect gas, the final temperature t is the same as the initial temperature t_0 . From (25) it appears that the velocity of efflux increases as the final pressure diminishes, becoming a maximum =

$$\sqrt{2 J C (a + t_0)} \quad \text{or} \quad \sqrt{\frac{2 k p_0 v_0}{k - 1}}$$

when the escape takes place into a vacuum ($p = 0$).

According to Carnot's conclusion, a proof of which will be given presently, the efficiency of such a cycle as the one just described is the same whatever the working substance; we may therefore, in order to determine the efficiency of the cycle, choose any material we please. The problem becomes simplest if we suppose the material to be a perfect gas. Then, the work done by the substance during operation 2 is, by (18),

$$W = R(a + t) \log \frac{v_3}{v_2},$$

and the heat taken in during the same operation is

$$Q = \frac{R(a + t)}{J} \log \frac{v_3}{v_2}.$$

The work done on the substance during the fourth operation is

$$W' = R(a + t') \log \frac{v_4}{v_1},$$

and the heat given out is

$$Q' = \frac{R(a + t')}{J} \log \frac{v_4}{v_1}.$$

The efficiency of the cycle is, therefore,

$$M = \frac{Q - Q'}{Q} = \frac{(a + t) \log \frac{v_3}{v_2} - (a + t') \log \frac{v_4}{v_1}}{(a + t) \log \frac{v_3}{v_2}};$$

but, since v_1 becomes v_2 as the result of an adiabatic compression during which temperature rises from t' to t , and v_3 becomes v_4 by an adiabatic expansion accompanied by fall of temperature from t to t' , we have, by (14),

$$\frac{v_1}{v_2} = \frac{v_4}{v_3}, \text{ and therefore } \frac{v_3}{v_2} = \frac{v_4}{v_1}.$$

It follows that the logarithms in the expression for M are all equal, and therefore that the expression reduces to

$$M = \frac{Q - Q'}{Q} = \frac{(a + t) - (a + t')}{a + t} = \frac{t - t'}{a + t}. \quad (27)$$

The result of (27) is, in words, that the efficiency of a cycle such as that described—known as a 'Carnot's cycle'—consisting of an adiabatic compression and an adiabatic expansion, alternating with an isothermal expansion and isothermal compression, is equal to the difference of the temperatures at which heat is taken in and given out respectively by the working substance (that is, the difference of the temperatures at which the two isothermal processes take place), divided by the temperature at which heat is taken in increased by the constant quantity a depending on the position of the zero-point of the thermometric scale employed. Before going further, it will be convenient to discuss a little more fully the physical significance of this constant.

It is implied in equation (6), $p v = R(a + t)$, which we have taken as the starting point for what has been said about the properties of perfect gases, that the thermometric scale is such that equal differences of temperature cause equal changes in the value of the product $p v$ for a constant quantity of a perfect gas. This is the same thing as saying that we agree to measure temperatures by a perfect gas thermometer, but it leaves us free to choose arbitrarily the size of the degrees and the zero-point of the scale. As to the former point, it is most convenient to define a degree of temperature as the one-hundredth part of the interval between the temperatures of melting ice and of saturated steam, both being under standard atmospheric pressure, and whenever the size of a degree comes into account in this article, this definition is to be understood. With regard to the position of the zero, it is evident that the natural zero of a perfect gas thermometer is the point at which the product $p v$ would vanish, that is, the point denoted by putting $t = -a$. From this it appears that the symbols T, T_1, T_2, \dots which we have hitherto used merely as abbreviations for $a + t, a + t_1, a + t_2, \dots$ may be interpreted as indicating the temperatures reckoned from the natural zero of the perfect gas thermometer which are respectively identical with those which, when reckoned from the arbitrary zero, are denoted by t, t_1, t_2, \dots . Consequently, expressing the temperatures at which heat is taken in and given out

Absolute Temperature.—Since, then, the efficiency of *any* reversible cycle is equal to the quotient of the difference between the temperatures at which heat is taken in and given out respectively divided by the temperature, counted from zero of the perfect gas thermometer, at which heat is taken in, the efficiencies of two cycles in which heat is received at the same temperature are to each other as the intervals of temperature occurring in the cycles. That is, if in two cycles heat is taken in at the same temperature T , and is given out in one cycle at T_1 and in the other at T_2 , we have:

$$\frac{T - T_1}{T - T_2} = \frac{M_1}{M_2}, \quad \text{or} \quad \frac{T_1 - T_2}{T - T_2} = \frac{M_2 - M_1}{M_2},$$

where M_1 and M_2 are the efficiencies of the respective cycles. If, however, W_1 and W_2 denote the amounts of work resulting from the reception of equal quantities of heat

by the working substances of the two cycles, $\frac{M_1}{M_2} = \frac{W_1}{W_2}$, and therefore

$$T_1 - T_2 = (T - T_2) \frac{W_2 - W_1}{W_2},$$

if we select arbitrarily two of the temperatures occurring in this formula, the third is defined by reference to them; moreover, since the formula contains only differences of temperature, it is equally applicable whatever the zero-point to which the temperatures are referred. Accordingly, if we take T to be the temperature of saturated steam under normal atmospheric pressure, and T_2 the temperature of melting ice under the same pressure, and agree that the numerical value of this interval shall be 100, we may write

$$T_1 - T_2 = 100 \frac{W_2 - W_1}{W_2}.$$

Lastly, if we take the temperature of melting ice as the zero-point of our scale, we have $T_2 = 0$, and therefore

$$T_1 = 100 \frac{W_2 - W_1}{W_2},$$

gives the temperature T_1 expressed by reference to what may be called the *absolute* centigrade scale. That is to say, the numerical value of the temperature T_1 is assigned relatively to the usual fixed points of the centigrade scale by means of the ratio of two quantities of work, a ratio which is expressible in terms of dynamical units (ergs), and does not involve a reference to the physical properties of any particular substance. The absolute scale of temperature thus arrived at was first proposed by Sir William Thomson. It is identical with the scale of the perfect gas thermometer, but the conception is of fundamental importance, since it affords a real method of comparing intervals of temperature by means of possible measurements with real substances, instead of a merely theoretical definition based on properties assigned to a hypothetical material.

Complex Cycles.—In the operations which constitute a Carnot's cycle, change of temperature and change of the quantity of heat in the working substance occur separately. But in ordinary circumstances both these changes take place together. It is evident, however, that a succession of very small changes of temperature, alternating with very small increments or decrements in the quantity of heat possessed by a body, may be made to resemble as closely as we please any reversible process wherein temperature and quantity of heat both change continuously and at the same time. Hence, in any case where such a process forms part of a cycle, it will not cause any finite difference in the result if we imagine it replaced by a sufficiently great number of sufficiently small alternate adiabatic and isothermal operations.

In a Carnot's cycle, taking a quantity of heat Q from a source at temperature T , and rejecting heat at T' , the amount transformed into work, namely $\frac{Q}{T} (T - T')$, is the same as the amount that would be transformed if the whole quantity of heat Q were subdivided into an infinite number of infinitely small parts, dQ , and each part were employed in a cycle worked between the same temperatures T and T' ; for the heat transformed into work by each such elementary cycle would be $\frac{dQ}{T} (T - T')$, and therefore the amount transformed by all together would be $\int \frac{dQ}{T} (T - T') = \frac{Q}{T} (T - T')$. Again, if the interval of temperature $T - T'$ be subdivided into an infinite number of infinitely small parts, dT , the effect of the complete cycle will be the same as the combined

effect of an infinite number of cycles of infinitesimal range, the first of which takes in the quantity of heat Q at T , and gives out $Q_1 = Q \frac{T_1}{T}$ at T_1 , while the second takes in Q_1 at T_1 , and gives out $Q_2 = Q_1 \frac{T_2}{T_1}$ at T_2 ; the third takes in Q_2 at T_2 and gives out $Q_3 = Q_2 \frac{T_3}{T_2}$ at T_3 , and so on, the last one taking in Q_n at T_n and giving out $Q' = Q_n \frac{T'}{T_n}$ at T' where $T - T_1 = T_1 - T_2 = \dots = T_n - T' = dT$. The truth of this becomes apparent if we consider that the quantity of heat given out during any one elementary cycle is just equal to the quantity taken in during the elementary cycle next in order of temperature, so that the nett result of all the elementary cycles taken together is a quantity Q taken in at T , and a quantity Q' given out at T' , no heat being either taken in or given out on the whole at intermediate temperatures. It follows, therefore, that the difference between the quantities of heat Q and Q' has been converted into work, just as would be the result of the original cycle. This conclusion may also be arrived at by considering the quantities of heat transformed by the several elementary cycles, namely $\frac{Q}{T} dT, \frac{Q_1}{T_1} dT_1, \dots$ the total amount transformed being the sum of all these; but since $\frac{Q}{T} = \frac{Q_1}{T_1} = \dots = \frac{Q_n}{T_n}$, the sum becomes $\frac{Q}{T} \int dT = \frac{Q}{T} (T - T')$.

If we now suppose both kinds of subdivisions that have been considered to be carried out at the same time, we shall have, instead of the single cycle, during which the finite quantity of heat Q is received from the source, and worked between the temperatures T and T' , which have a finite difference, an infinite number of cycles each taking in an infinitesimal quantity of heat and working through an infinitesimal range of temperature; but the combined effect of the infinitely small cycles will be identical with that of the original finite cycle.

Similarly, any reversible cycle, even if including operations during which change of temperature and loss or gain of heat take place simultaneously, may be regarded as made up of an infinite number of infinitesimal Carnot's cycles, such that the temperatures at which heat is taken in and given out, and the nett quantities of heat taken in and given out at those temperatures, are the same for the combined infinitesimal cycles as for the single finite cycle.

General expression for Reversible Cycles.—It was shown above [equation (28)], that in a Carnot's cycle working between the absolute temperatures T and T' , a quantity of heat Q being taken in at the former temperature, and a quantity Q' given out at the latter, the following relation holds:

$$\frac{Q}{T} = \frac{Q'}{T'}$$

Or, reckoning heat given out as a negative quantity taken in:

$$\sum \left(\frac{Q}{T} \right) = 0.$$

We have now seen that any reversible cycle may be looked upon as built up from an infinite number of infinitesimal cycles. To each of these elementary cycles taken separately, the result just pointed out must apply, and therefore it must apply to all of them taken together. We may therefore write the following equation as applicable to every reversible cycle:

$$\int \frac{u}{T} = 0 \quad \dots \quad (29)$$

Condition of Maximum Efficiency of a Reversible Cycle.—The quantity of heat transformed into work in a complex cycle may be expressed by

$$Q_1 \frac{T_1 - T_1'}{T_1} + Q_2 \frac{T_2 - T_2'}{T_2} + Q_3 \frac{T_3 - T_3'}{T_3} + \dots$$

where the separate terms represent the quantities transformed by the several simple cycles, which together make up the complex cycle. If T and T' respectively represent the highest and lowest temperatures occurring during the cycle, it is evident that the sum of the above terms is less than $(Q_1 + Q_2 + \dots) \frac{T - T'}{T}$, which would express the quantity of heat transformed, if the whole quantity taken in during the cycle were taken in at the

highest temperature T , and if the whole quantity given out were given out at the lowest temperature T .

From this it appears that, in order to get as much work as possible from a given quantity of heat supplied to a steam-engine, or other contrivance for transforming heat into work, the supply of heat should take place at as high a temperature, and the withdrawal of heat at as low a temperature, as possible.

APPLICATION OF THERMODYNAMIC PRINCIPLES.

Many important consequences may be deduced from the two fundamental principles discussed in the preceding paragraphs. The first principle tells us that, when heat is transformed into work, the work done bears a constant ratio to the quantity of heat that disappears; the second enables us to determine the proportion of a given quantity of heat which undergoes transformation under definite conditions. Combining the two, we are able, in relation to many physical processes to establish equations which exhibit on one side the work done during the processes expressed in terms of mechanical quantities, while on the other side we have equivalent expressions in terms of thermal quantities.

Relations between the Thermal Coefficients.—Of the nine coefficients introduced at the beginning of this article for the purpose of expressing the thermal relations of different bodies, only α , the coefficient of expansion, ϵ , the coefficient of elasticity, and C , the specific heat under constant pressure, have hitherto been made the subjects of direct experimental determination. It is therefore essential, if the formulæ in which these coefficients occur are to have any definite meaning, that their values should be known in terms of the three coefficients already mentioned. We proceed to show how this knowledge can be arrived at.

We recall in the first place the following relation between the coefficient of increase of pressure β , and the coefficients α and ϵ , equation (4), namely:

$$\beta = \frac{\alpha \epsilon}{p}$$

Considering now an infinitesimal Carnot's cycle, we have as the thermal expression for the work done, $J dQ \frac{dT}{T}$, and as the mechanical expression for the same, $dp dv$; whence the equation

$$J dQ = \frac{T}{dT} dp dv.$$

But here dQ is the quantity of heat taken in during a small isothermal increase of volume dv at the temperature T : hence, by (5a), we have $dQ = l dv$. Also, to determine dp , the amount by which the pressure during expansion exceeds the pressure during compression, we have $dp = \frac{dp}{dT} dT$, where $\frac{dp}{dT}$ is the rate of change of pressure with temperature when volume is constant. Introducing these values into the above equation, we get:

$$J l dv = \frac{T}{dT} \cdot \frac{dp}{dT} \cdot dT \cdot dv$$

or

$$\begin{aligned} l &= \frac{T}{J} \cdot \frac{dp}{dT} \cdot \dots \dots \dots \\ \text{by (2)} \quad &= \frac{T}{J} p \beta = \frac{T}{J} \alpha \epsilon \dots \dots \dots \end{aligned} \quad \left. \vphantom{\begin{aligned} l &= \frac{T}{J} \cdot \frac{dp}{dT} \cdot \dots \dots \dots \\ &= \frac{T}{J} p \beta = \frac{T}{J} \alpha \epsilon \dots \dots \dots \end{aligned}} \right\} (30)$$

Combining equations (5a) and (5b), and putting $dp = 0$, we have

$$C - c = l \frac{dv}{dv} = l v \alpha$$

by (30)

$$= \frac{T}{J} \frac{\alpha^2 \epsilon}{p} \dots \dots \dots (31)$$

if $\rho = \frac{1}{v}$ is put for the density (mass of unit volume) of the substance,

Putting $dt=0$, equations (5a) and (5b) give

$$h = l \frac{dv}{dp} = - l \frac{v}{\epsilon} \\ = - \frac{T}{J} \frac{\alpha}{\rho} \quad \dots \quad (32)$$

In the same way (5a) and (5c) give

$$c dt + l dv = \kappa dp + \lambda dv;$$

whence, if $dv=0$,

$$\kappa = c \frac{dt}{dp} = \frac{c}{p \beta} = \frac{c}{\alpha \epsilon}$$

or, by (31),

$$\kappa = \frac{C}{\alpha \epsilon} - \frac{T}{J} \frac{\alpha}{\rho} \quad \dots \quad (33)$$

and (5b) and (5c), if $dp=0$, give

$$\lambda = C \frac{dt}{dv} = C \frac{1}{\alpha v} = C \frac{p}{\alpha} \quad \dots \quad (34)$$

Coefficient of Adiabatic Elasticity.—The coefficient of volume-elasticity of a substance is defined as $-v \frac{dp}{dv}$, but the ratio $dp : dv$ depends not only on the nature of the substance, but also, as already pointed out in the case of gases, upon the thermal conditions to which it is subject. If temperature remains constant, the above expression represents the coefficient of isothermal elasticity, ϵ . Its value is given by (5a) and (5b), which, if $dt=0$, yield

$$\epsilon = -v \frac{dp}{dv} = -v \frac{h}{l}.$$

The coefficient of adiabatic elasticity E is given by (5c) on putting $dQ=0$, namely,

$$E = -v \frac{dp}{dv} = v \frac{\lambda}{\kappa};$$

which, on substituting the values of λ and κ from (34) and (33), becomes

$$E = \frac{\epsilon}{1 - \frac{T}{J} \frac{\alpha^2}{C \rho}} \quad \dots \quad (35)$$

or, when the multiplier of ϵ in the denominator of this expression is a small quantity, as it usually is in the case of solids and liquids, we have approximately

$$E = \epsilon \left(1 + \frac{T \alpha^2}{J C \rho} \right) \quad \dots \quad (35')$$

Dividing (35) by ϵ , we get for the ratio of the coefficients of adiabatic and isothermal elasticity

$$\frac{E}{\epsilon} = \frac{1}{1 - \frac{T \alpha^2}{J C \rho}} \quad \dots \quad (36)$$

But it will be seen from equation (31) that this is the ratio of the specific heat under constant pressure to the specific heat at constant volume. Hence, for all bodies, the ratio of the two elasticities is equal to the ratio of the two specific heats, or

$$\frac{E}{\epsilon} = \frac{C}{c} \quad \dots \quad (37)$$

The various thermal coefficients, as well as the coefficient of adiabatic elasticity, have thus been expressed in terms of the three which can most easily be made the subject of direct measurement. The expressions now given are of general application, and include, as special cases, the formulæ given above (p. 1927) as applying to perfect gases. This follows at once from the relation $T \alpha = 1$, α being the coefficient of expansion of a perfect gas.

Absolute Scale of Temperature.—As already explained, the temperatures denoted in the above formulæ are supposed to be measured by a perfect gas thermometer, and reckoned from the natural zero of such a scale. But, inasmuch as no known substance possesses the properties attributed to a perfect gas, a perfect gas thermometer can be

only an ideal instrument. If, however, we can ascertain how far the properties of a real gas differ from those of an ideal perfect gas, statements of temperature referred to a thermometer filled with this gas can be translated into the corresponding values referred to a thermometer constructed with a perfect gas. Experiments having this object in view have been carried out by Dr. Joule and Sir William Thomson (*Phil. Trans.* 1854, p. 321; 1862, p. 579). Their method was to force a gas in a continuous stream through a porous plug offering so much resistance to its passage that the gas escaped from the plug with only a negligible velocity, even when the difference of pressures on the two sides of the plug was considerable. If, during such an experiment, the gas does not lose or gain heat, it appears, from (24), that, in the case of a perfect gas, there would be no change of temperature—the final result being simply that the pressure of the gas is diminished and its volume increased by its passage from one side of the plug to the other. Accordingly, since no internal work is done during increase of volume of a perfect gas, no heat is used up and no change of temperature takes place. In the gases experimented upon, a slight change of temperature was always observed—namely, a fall of temperature in the case of air, nitrogen, oxygen, and carbonic acid, and a very slight rise in the case of hydrogen. The alteration of temperature for a given gas was found to be proportional to the change of pressure, and smaller at high temperatures than at low temperatures. By determining the ratio of the change of temperature to the change of pressure undergone by a gas under these circumstances, data were obtained by means of which, in conjunction with other data respecting the properties of gases derived chiefly from Regnault's observations, it is possible to give numerical statements of temperatures which do not depend upon the special properties of any particular substance. The following statement of the reasoning by which this result is arrived at is essentially abridged from Sir William Thomson's article *HEAT* in the *Encyclop. Britan.* 9th ed. xi.

Consider in the first place a series of four operations constituting a closed cycle performed on any substance as follows:—

(1.) Alter the bulk or shape of the substance till it becomes warmer to any desired degree. (2.) Keeping it now at this higher temperature, alter bulk or shape further, and generate the heat which the substance takes to keep its temperature constant, by stirring water, or a portion of the substance itself if it is partly fluid, and measure the quantity of work spent in this stirring. (3.) Bring the substance back towards its original bulk and shape till it becomes cooled to its original temperature. (4.) Keeping it at this temperature, reduce it to its original bulk and shape, carrying off, by a large quantity of water, the heat which it must part with to prevent it becoming warmed. Find by a special experiment how much work must be done to give an equal amount of heat to an equal amount of water by stirring. Then the ratio of the first measured quantity of work to the second is the ratio of the higher temperature to the lower on the absolute thermodynamic scale.

It will be seen that the definition of absolute temperature given in this paragraph agrees with that already given in this article, but that it is put in a more general form. If we suppose the changes of temperature taking place in operations (1) and (3) to be infinitely small, the corresponding changes of stress will also be infinitely small. If we suppose the stress upon the working substance to be a uniform pressure over the whole surface, and that its average amount during the second operation is p , its average value during the fourth operation will be $p \mp dp$, or infinitely near to its value during the second (the *plus* sign would apply in the case of substances such as water below 4° C., or a mixture of water and ice, whose temperature is *lowered* by *increase* of pressure); if, further, the change of bulk during the second operation is denoted by u , the work done during this operation will be $w = pu$, and it will exceed the work done during the fourth operation by an amount $dw = u dp$. This then is the amount by which the work done by the substance upon external bodies during the whole cycle exceeds the work done by them upon it. We may, therefore, in accordance with equation (28), write

$$\frac{dT}{T} = \frac{dw}{w} = \frac{u dp}{w},$$

or, multiplying numerator and denominator by p ,

$$\frac{dT}{T} = \frac{p u}{w} \cdot \frac{dp}{p} \quad \dots \quad (38)$$

The first factor on the right-hand side of this equation, called by Sir W. Thomson the 'work ratio,' expresses the ratio of the work done by the working substance upon external bodies during the second operation of the above cycle, to the total amount of work done upon it: the statement of the equation may therefore be put into words as follows:—

The ratio of the infinitesimal rise of temperature to the whole absolute temperature is equal to the work-ratio multiplied into the ratio of the infinitesimal increase of stress to the whole stress.

As a special example of the application of definition of absolute temperature in this form, consider any substance subject to uniform pressure in all directions. Let p and v be its pressure and volume, and let e be the energy which must be given to it to bring it from any conveniently defined zero condition, which we may call the condition $(p_0 v_0)$, to the given condition $(p v)$. Let heat be communicated to the substance so as to cause its volume to increase by dv , the pressure being kept constant. The energy of the body will thus become greater by the amount $\frac{de}{dv} \cdot dv$. At the same time, the body in expanding and pressing out the matter around it does work to the extent $p dv$, and therefore the whole quantity of work required to generate the heat given to it must be $\left(\frac{de}{dv} + p\right)dv$.

Consequently the work-ratio is $\frac{p}{\frac{de}{dv} + p}$, and therefore by (38)

$$\frac{DT}{T} = \frac{dp}{p} \cdot \frac{p}{\frac{de}{dv} + p} = \frac{dp}{\frac{de}{dv} + p} \quad (39)$$

where DT denotes the change of temperature due to the increase of pressure dp , the substance being prevented the while from either losing or gaining heat. The last condition implies that the change of energy of the body is equal to the work done upon it by pressure from without, or

$$\frac{de}{dv} dv + \frac{de}{dp} dp = -p dv,$$

the negative sign on the right meaning that the change of volume dv is negative if the change of pressure dp is positive. Hence

$$dv = \frac{-\frac{de}{dp}}{\frac{de}{dv} + p} dp.$$

But

$$DT = \frac{dT}{dp} dp + \frac{dT}{dv} dv,$$

or, by the last equation,

$$DT = \left(\frac{dT}{dp} - \frac{\frac{dT}{dv} \cdot \frac{de}{dp}}{\frac{de}{dv} + p} \right) dp.$$

Eliminating $\frac{DT}{dp}$ from this by (39), we get

$$T = \left(p + \frac{de}{dv} \right) \frac{dT}{dp} - \frac{de}{dp} \cdot \frac{dT}{dv} \quad (40).$$

To connect this result with the experiments on the passage of fluids through a porous plug, we may proceed as follows:—Let $p + \delta p$ be the constant pressure on the fluid before passing the plug, and p the pressure on it beyond the plug. If, as is the case with common air, nitrogen, oxygen, carbonic acid, and no doubt many other gases, the fluid leaves the plug cooler than it enters it, let δw be the amount of work which, spent in stirring the fluid flowing from the plug, would restore unit-mass of it to the original temperature. If, on the other hand, the fluid is warmed by passing the plug, as is the case with hydrogen and all ordinary liquids, let δw denote the work that must be done in stirring water in order to warm it as much as it would be warmed if employed to cool unit-mass of the fluid on the second side of the plug to the temperature which it had on the first side. In this case δw is to be reckoned negative, as it is the mechanical equivalent of heat taken away from the fluid to restore its original temperature. Let v and $v + \delta v$, e and $e + \delta e$, respectively, represent the volume and energy of unit-mass of the fluid before and after passing the plug, the symbols in each case being understood as referring to the fluid in the tranquil parts of the stream

where it is unaffected by the rapids caused by the plug or by the eddies due to the stirring. Then the work done upon the fluid while approaching the plug, and done by it while flowing away from the plug, will be the same as if it were pressed towards the plug by a piston exerting a constant pressure $p + \delta p$ per unit of surface, and a piston exerting a constant pressure p were pushed forward by the escaping fluid. The work done by the first piston upon unit-mass of the fluid would be $(p + \delta p)(v + \delta v)$, and that done upon the second by the same quantity of fluid $p v$. The whole quantity of work done on unit-mass of the fluid therefore exceeds the work done by it by

$$(p + \delta p)(v + \delta v) - p v + \delta w = p \delta v + v \delta p + \delta w,$$

and this consequently must be the gain of energy by the fluid, or the amount by which e , the energy per unit-mass beyond the plug, exceeds $e + \delta e$, the energy per unit-mass of the fluid approaching the plug: that is,

$$- \delta e = p \delta v + v \delta p + \delta w. \quad (41)$$

Now the combined effect of the plug and the stirring is to make the temperature of the fluid the same, notwithstanding the change of pressure from $p + \delta p$ to p , and the change of volume from $v + \delta v$ to v ; in other words, the changes of temperature corresponding to the changes of pressure and of volume taken separately are such as to compensate each other, or

$$\delta T = \frac{dT}{dp} \delta p + \frac{dT}{dv} \delta v = 0;$$

that is,

$$\delta v = - \frac{dT}{dp} \div \frac{dT}{dv} \delta p,$$

and the change of energy may be written

$$\delta e = \frac{de}{dp} \delta p + \frac{de}{dv} \delta v.$$

Putting these values of δv and δe into equation (41), and at the same time dividing by δp , we get

$$\left(p + \frac{de}{dv} \right) \frac{dT}{dp} \div \frac{dT}{dv} - \frac{de}{dp} = v + \frac{\delta w}{\delta p}.$$

Combining this with (40), we have

$$T + \frac{dT}{dv} = v + \frac{\delta w}{\delta p},$$

or, dividing by v and taking reciprocals of both members,

$$\frac{v}{T} \frac{dT}{dv} = \frac{1}{1 + \frac{1}{v} \frac{\delta w}{\delta p}}. \quad (42)$$

This shows that if, for any one fluid, and for some one value of the pressure p , the heating or cooling effect due to passage through the porous plug were at all temperatures to be nothing, so that the work δw required to undo the change of temperature should vanish, then for this fluid

$$\frac{v}{T} \frac{dT}{dv} = 1$$

or, by integration,

$$T = B v \quad (43)$$

where B is an arbitrary constant. From this we infer that, with this particular fluid for thermometric substance, with the particular pressure of the experiment, and throughout the range of temperature for which the result $\delta w = 0$ has been obtained, absolute temperature is shown on a scale graduated and numbered in simple proportion to the whole volume of fluid.

Now Joule and Thomson's experiments showed that for pressures of from one to five or six atmospheres, hydrogen, air, nitrogen, oxygen, and carbonic acid, all somewhat nearly fulfil the condition of passing through a porous plug without change of temperature—hydrogen much more nearly, and carbonic acid much less nearly than any of the others. Hence we infer that absolute temperature is somewhat nearly proportional to the volume of the fluid, if any one of those gases is used in a constant-pressure thermometer. Further, since we know from the experiments of Regnault and others that the ratio in which volume changes under constant pressure, for a

given alteration of temperature, is nearly the same for these gases (at least, leaving out carbonic acid) as the ratio in which pressure changes at constant volume for the same alteration of temperature, we also infer that absolute temperatures are somewhat approximately shown by a thermometer graduated so as to show the pressure of one of these gases when kept at constant volume.

We see, then, that the assumption commonly made, that temperatures measured by an air or gas thermometer are approximately absolute temperatures, is justified.

To determine the degree of approximation that can be thus made, we must return to equation (42). The quantity of work, δw , required to undo the cooling effect can in practice be most accurately estimated by help of the specific heat of the fluid and the mechanical equivalent of heat. If C be the specific heat under constant pressure, and J the mechanical equivalent, we have

$$\delta w = JC \delta T,$$

and therefore (42) becomes

$$\frac{v}{T} \frac{dT}{dv} = \frac{1}{1 + \frac{JC}{v} \frac{\delta T}{\delta p}} \quad \dots \quad (44)$$

It is to be noted here that the change of temperature δT can only be expressed in arbitrary measure, as we have not yet established a natural system of thermometry; it is, however, sufficient for our reasoning that J shall denote the dynamical equivalent of a water-gram-degree, upon the same thermometer as that upon which the interval δT is measured.

The experiments showed δT to be simply proportional to δp , not only for infinitesimal differences of pressure, but for differences amounting to 5 or 6 atmospheres. In the case of hydrogen, the observed effect was an increase of temperature (δw therefore negative) amounting, on an average of the experiments at different temperatures, to 0.039 of a degree centigrade for a difference of pressure on the two sides of the plug equal to the pressure due to a column of ice-cold mercury 76 cm. in height.

Denoting this pressure by Π , we have then $\frac{\delta T}{\delta p} = -\frac{0.039}{\Pi}$, whence

$$\frac{v}{T} \frac{dT}{dv} = \frac{1}{1 - 0.039 \frac{JC}{\Pi v}}$$

Writing this

$$\frac{dT}{T} = \frac{dv}{v - 0.039 \frac{JC}{\Pi}}$$

we get by integration

$$T = B \left(v - 0.039 \frac{JC}{\Pi} \right) \quad \dots \quad (45)$$

Now let T_0 denote the absolute temperature corresponding to 0° C., T_{100} the absolute temperature corresponding to 100° C., and let v_0 and v_{100} be the volumes occupied by unit-mass of hydrogen at the same two temperatures when under any constant pressure (say, from 1 to 5 or 6 atmospheres) within the limits of Joule and Thomson's experiments, then (45) gives

$$T_0 = B \left(v_0 - 0.039 \frac{JC}{\Pi} \right) \quad \text{and} \quad T_{100} = B \left(v_{100} - 0.039 \frac{JC}{\Pi} \right)$$

whence

$$\frac{T_{100} - T_0}{T_0} = \frac{v_{100} - v_0}{v_0 - 0.039 \frac{JC}{\Pi}} \quad \dots \quad (46)$$

If we make $T_{100} - T_0 = 100$ and put H for $\frac{v_{100} - v_0}{v_0}$, the expansion of hydrogen under constant pressure, from 0° to 100° C. referred to the volume at 0° taken as unity, (46) gives

$$T_0 = \frac{100}{H} \left(1 - 0.039 \frac{JC}{\Pi v_0} \right).$$

If V_0 denote the volume of unit-mass of hydrogen under pressure Π instead of under the actual pressure p , this becomes

$$T_0 = \frac{100}{H} \left(1 - \frac{V_0}{v_0} 0.039 \frac{JC}{\Pi V_0} \right) \quad \dots \quad (47)$$

To obtain the numerical value of T_0 from (47), we have the following data :

H, for hydrogen under constant pressure of 1 atmosphere = .36613,

whence $\frac{100}{H} = 273.13$ (Regnault),

C = 3.409 (Regnault),

J = 4.175×10^7 ergs. (Joule),

$\Pi V_0 = 1.1316 \times 10^{10}$ (Regnault).

Putting in these numbers, we get

$$T_0 = 273.13 \left(1 - 0.00049 \frac{V_0}{v_0} \right)$$

or, since the pressure under which expansion takes place is supposed to be atmospheric, and therefore $v_0 = V_0$,

$$T_0 = 273.00.$$

The experiments on air lead to almost an identical value for T_0 , and those on carbonic acid to one not very different. In each of these gases, passage through the porous plug caused a lowering of temperature, which was found to vary very nearly in the inverse proportion to the square of the temperature C, by mercury thermometer, with 273 added. Hence nearly enough for use in the small term of the denominator of (44)

$$\frac{\delta T}{\delta p} = A \left(\frac{273}{T} \right)^2 \frac{p}{\Pi} \quad (49)$$

where T denotes, as before, absolute temperature, and A the amount of the cooling effect per atmosphere difference of pressure on the two sides of the plug, at the temperature of melting ice. The values of A found for air and carbonic acid are 0.275 and 1.388 respectively. As the proper mean value to apply between 0° and 100° C., Sir W. Thomson calculates 0.756 A, which gives 0.208 for air, and 1.049 for carbonic acid, as the factors to be substituted for -0.039 in (47) to make it apply to these gases. As to the other data, we have

H = 0.36706 for air, 0.3710 for carbonic acid

C = .2375 " .2006 (mean sp. ht. from 0° to 100°)

$\Pi V_0 = 7.84 \times 10^8$ " 5.13×10^8 " " "

Using these numbers, and taking $v_0 = V_0$, we get

$$\begin{aligned} T_0 &= \frac{100}{.36706} (1 + .0026) = 272.14 \times 1.0026 \\ &= 273.14 \text{ (by air),} \end{aligned}$$

and

$$\begin{aligned} T_0 &= \frac{100}{.3710} (1 + .0171) = 269.5 \times 1.0171 \\ &= 274.15^* \text{ (by carbonic acid).} \end{aligned}$$

Of the three values thus arrived at for the absolute temperature of melting ice, Sir W. Thomson regards that derived from air as the most trustworthy on account of the greater ease, and therefore probably greater accuracy, with which the requisite numerical data can be determined in the case of air as compared with the other gases. The true temperature of melting ice may therefore be taken as 273.1 from absolute zero. The meaning of this result is that the ratio of the absolute temperature at which saturated water-vapour has a pressure equal to that of 76 cm. of ice-cold mercury to the absolute temperature of melting ice is 373.1 : 273.1.

Determination of Absolute Temperature by Observations with a Constant-Pressure Air Thermometer.—The temperature of melting ice being known, it is easy to deduce a formula to express the temperature in degrees of the absolute centigrade scale at which a quantity of air measuring v_0 c.c. at 0° C. occupies any observed volume v under the same pressure. For this purpose, we first generalise equation (45) by putting, instead of the numerical factor -0.039 applicable to hydrogen, the symbol m to stand for the mean cooling effect, corresponding to the range of temperature in question, produced in any gas when the difference of pressure on the two sides of the

* This number differs slightly from that calculated by Sir W. Thomson (*op. cit.* 573), namely 273.9. Thomson takes the mean cooling effect for carbonic acid as 1.105, which seems inconsistent with his own data, and finds 1.0163 for the final multiplier of $\frac{100}{.371}$.

plug is Π (1 atmosphere). m is to be reckoned negative when, as with hydrogen, the gas is heated by passing through the plug; its value at any temperature t reckoned from zero centigrade is nearly $m = \frac{1}{2} A \left[1 + \left(\frac{273}{273+t} \right)^2 \right]$ given by (49), the value of t being known, accurately enough for use in this formula, by a mercurial thermometer. We thus get

$$T = B \left(v + m \frac{J C}{\Pi} \right) \quad . \quad . \quad . \quad (50)$$

which gives, as in (46),

$$\frac{T - T_0}{T_0} = \frac{v - v_0}{v_0 + m \frac{J C}{\Pi}} = \frac{v - v_0}{v_0} \cdot \frac{1}{1 + m \frac{J C}{\Pi v_0}}$$

whence

$$t = T - T_0 = T_0 \frac{v - v_0}{v_0} \left(1 - m \frac{J C}{\Pi V_0} \cdot D \right) \quad . \quad . \quad (51)$$

where $D = \frac{V_0}{v_0}$ is the relative density of the gas at 0° C. referred to the density of the same gas at 0° and under atmospheric pressure, Π , taken as unity. Putting in numerical values and making Π one atmosphere, and therefore $D = 1$, we obtain from (51)

$$t = 273.1 \frac{v - v_0}{v_0} (1 - 0.0126 m).$$

This formula applies, with the proper value of m , to air, oxygen, hydrogen or nitrogen, the value of $\frac{C}{V}$, or the specific heat of the quantity of gas occupying unit-volume (1 c.c.) at 0° C., and under atmospheric pressure being nearly the same for all of these gases according to Regnault. For $t = 100^\circ$, the value of m is -0.039 for hydrogen, $+0.208$ for air, $+0.253$ for oxygen, and 0.249 for nitrogen.

Another formula for use with a constant-pressure gas thermometer is easily derived from (51), namely,

$$\begin{aligned} t &= 100 \frac{v - v_0}{v_{100} - v_0} \left[1 - \frac{J C}{\Pi V_0} D (m - m_{100}) \right] \\ &= 100 \frac{v - v_0}{v_{100} - v_0} [1 - 0.0126 D (m - m_{100})] \end{aligned}$$

where v_{100} is the volume assumed by the gas at 100° C., m the mean cooling effect for the interval of temperature 0° C. to t , and m_{100} the value for the interval 0° to 100° C.

Hitherto the constant-pressure gas thermometer has not been constructed in a form convenient for practical use. Sir William Thomson, however, has designed and given a detailed description of such an instrument (*op. cit.* 575, 576), as to which he says, 'It seems probable that the constant-pressure hydrogen or nitrogen gas thermometer, which we have now described, may give even more accurate thermometry than Regnault's constant-volume air thermometers, and it seems certain that it will be much more easily used in practice.'

Constant-volume Air Thermometer.—A constant-volume air thermometer was employed by Prof. Rowland for reducing to absolute values the temperature-observations connected with his determination of the mechanical equivalent of heat (see above, p. 1926). If we put θ for the temperature directly indicated by the instrument itself without correction to the absolute scale—that is, if we make $\theta = 100 \frac{p - p_0}{p_{100} - p_0}$, where p_0 , p_{100} , and p are the pressures exerted by the constant volume of gas in the thermometer at 0° , 100° , and the temperature t to be determined respectively, the formula deduced by Rowland from Joule & Thomson's experiments may be written

$$t = T - T_0 = \theta - 0.00088 \theta \frac{100 - \theta}{273 + \theta}.$$

By means of this formula, Rowland has calculated the following table for reducing the readings of the constant-volume air thermometer, containing air of normal density, to the equivalent temperatures on the absolute scale counted from 0° C.

Reading of air-thermometer θ	Absolute temperature above 0° C. $t = T - T_0$	Correction to air-thermometer readings $t - \theta$
0°	0	0
10	9.9972	-0.0028
20	19.9952	-0.0048
30	29.9939	-0.0061
40	39.9933	-0.0067
50	49.9932	-0.0068
60	59.9937	-0.0063
70	69.9946	-0.0054
80	79.9956	-0.0044
90	89.9978	-0.0022
100	100.000	0.0
200	200.037	+0.037
300	300.092	+0.092
400	400.157	+0.157
500	500.228	+0.228

Latent Heat.—The value of the coefficient that we have represented by the symbol l , or the 'latent heat of expansion,' is given by equation (30), as $\frac{T}{J} \cdot \frac{dp}{dT}$. Its physical meaning appears from (5a), namely $dQ = c dt + l dv$, and may be stated to be the quantity of heat required to cause unit increase of volume at constant temperature. The term latent heat, however, in its most usual sense means the quantity of heat that must be given to unit-mass of a substance to cause a change of condition at constant temperature and pressure. Let L stand for latent heat in this sense, and let u be the change of volume taking place during change of state of unit-mass. We then get immediately

$$L = ul,$$

or, by (30),

$$L = u \frac{T}{J} \frac{dp}{dT} \quad (52)$$

The value of u may evidently be written $u = s_2 \cdots s_1$, if s_1 be put for the volume of unit-mass of the substance in its first state, and s_2 for the volume of unit-mass in the second state, that is, the state into which it is transformed by *receiving* heat.

Application to Water-vapour. The extent of agreement between this formula and the results of observation can be tested most satisfactorily in the case of water, as the data required for applying it are better known for water than for any other substance. Fairbairn & Tate's experiments (*Phil. Trans.* 1860; also iii. 97 of this work) give the value of s , for saturated steam for a considerable range of temperature, and Regnault's experiments give the means of determining the values of $T \frac{dp}{dT}$. Tables of this latter quantity have been calculated from Regnault's results by Count P. de Saint-Robert (*Principes de Thermodynamique*, Turin, 1870), and his numbers are employed in the following comparison.

Latent Heat of Water-vapour.

Temperature	α	$T \frac{dp}{dT}$	L calculated	L Regnault
273 + 58.2	8274.3	2905.5	565.7	565.9
" 68.5	5332.5	4455.9	557.8	558.7
" 77.5	3714.1	6314.0	551.8	552.4
" 86.8	2622.4	8854.1	546.3	545.8
" 92.7	2148.5	10859.0	549.0	541.6
" 117.2	942.1	52404.1	518.8	524.3
" 139.2	496.2	42506.5	496.8	508.6
" 144.7	432.1	48766.4	496.9	504.6

It will be seen that the agreement between the calculated and experimental values of

L is such as to afford a striking confirmation of the reasoning employed in deducing equation (52).

Internal Latent Heat.—In general, change of volume takes place during change of state of aggregation, and therefore work, equal in amount to the product of the change of volume into the average pressure under which it occurs, is done either by or upon the body, and the mechanical equivalent of this work is included in the value of L as given above, together with what may be called the internal or true latent heat, that is, the heat consumed in overcoming internal molecular forces. Accordingly, putting r for the internal latent heat,

$$r = L - \frac{1}{J} \int_0^u p du$$

Or, when the change takes place under constant pressure

$$r = L - \frac{p}{J} u.$$

From this expression we may eliminate either L or u by means of (52) and write either

$$\begin{aligned} r &= \left(T \frac{dp}{dT} - p \right) \frac{u}{J} \\ \text{or} \quad r &= L \left(1 - \frac{p}{T \frac{dp}{dT}} \right) \frac{u}{J} \end{aligned} \quad (53)$$

Latent heat of Dissociation.—The process of gradual decomposition with rise of temperature, or diminution of pressure, or both, to which the term 'dissociation' was applied by Deville (vi. 425, vii. 636, viii. 1009), is exactly analogous, from a physical point of view, to the process of evaporation, and equation (53) applies directly to these phenomena, r being the quantity of heat required to dissociate unit-mass of substance at absolute temperature T under pressure p , and u the difference between the volume at this temperature and pressure of the dissociated products and the volume of unit-mass of the original substance.

The quantity of heat r usually includes heat spent in causing change of physical state as well as that spent strictly in causing chemical decomposition. When the former quantity is known, the latter can be found by subtraction. For example, when aqueous vapour is formed from (say) dilute sulphuric acid, part of the heat required for its formation goes to cause vaporisation, and the remainder to cause dissociation of the water from the acid. Let r be the total internal latent heat required for the formation of 1 gram of water-vapour from dilute sulphuric acid at absolute temperature T , and let p be the maximum pressure of the vapour given off by the acid at this temperature, and u the volume occupied by 1 gram of vapour at temperature T and under pressure p ; also, let r_1 , p_1 , and u_1 have corresponding meanings in the case of pure water. Then we have

$$r = \left(T \frac{dp}{dT} - p \right) \frac{u}{J} \quad \text{and} \quad r_1 = \left(T \frac{dp_1}{dT} - p_1 \right) \frac{u_1}{J},$$

and therefore for the heat spent in causing purely chemical change

$$r - r_1 = \frac{1}{J} \left[\left(\frac{dp}{dT} - \frac{dp_1}{dT} \right) T - (pu - p_1u_1) \right]$$

In the particular case selected for illustration, p_1 is rather less than p , and u_1 rather greater than u ; hence, at any rate for any considerable degree of dilution, $pu - p_1u_1$ cannot differ much from zero, and we may write approximately

$$r - r_1 = \frac{T}{J} \left(\frac{dp}{dT} - \frac{dp_1}{dT} \right)$$

for the heat required to separate 1 gram of water from dilute sulphuric acid.

Specific Volume of saturated Vapour.—If the latent heat of vaporisation at a given temperature T is known by direct experiment, and also the values of $\frac{dp}{dT}$ at the same temperature, equation (52) gives

$$u = s_2 - s_1 = \frac{JL}{T} \cdot \frac{dT}{dp}$$

as the difference between the specific volume s_1 of the liquid and s_2 that of the vapour

at temperature T . The former being known by experiments on the expansion of the liquid, the latter can be at once calculated.

Limit of the Liquid State. Critical Temperature.—If s_1 be the specific volume of a liquid and s_2 that of the corresponding saturated vapour, s_1 continually increases (except in a few cases, such as that of water below 4°C .) and s_2 continually decreases as temperature rises. Hence at some sufficiently high temperature we must have $s_1 = s_2$. At this temperature we have $u = 0$, and therefore (equation 52) $L = 0$. Consequently the state of vapour is here continuous with the liquid state, inasmuch as the passage from one to the other takes place without change of density or the absorption of heat. The temperature at which this occurs is called by Dr. Andrews the 'critical temperature.'

Influence of Pressure on Melting-point.—Another application of the same fundamental formula (52) as that from which the last results are derived shows that in general the melting point of a solid body must change with the pressure to which it is subject. The factors J , L , and T being all positive, it follows that $\frac{dT}{dp}$ must be of the same sign as u ; that is, when u is positive (specific volume of liquid greater than that of solid), dT must be of the same sign as dp , or the melting point must rise with increase of pressure; on the other hand, if u is negative (sp. volume of liquid less than that of solid), the melting point must fall with increase of pressure. This remarkable result was first pointed out by Professor James Thomson in 1849 in the case of ice, and was verified experimentally in the following year by Sir William Thomson (J. Thomson, *Edinb. Roy. Soc. Trans.* 1849, xvi. 1; W. Thomson, *Edinb. Roy. Soc. Proc.* February 1850; *Phil. Mag.* 1850, [3], xxxvii. 123).

If s_1 denote the specific volume of ice at 0°C ., s_2 the specific volume of water at the same temperature, and L the latent heat of fusion of ice, equation (52) gives

$$\frac{dT}{dp} = \frac{(s_2 - s_1)T}{JL} \quad (54)$$

According to Rossetti (vi. 672) the density of water at 0° compared with water at 4° is 0.999871, and according to W. H. Miller its absolute density at 4° is 1.000013. Hence for s_2 we have

$$s_2 = \frac{1}{1.000013 \times 0.999871} = 1.000116.$$

The value of s_1 is given by Bunsen's determination (vi. 681) of the relative density of ice at 0° , namely 0.91674, whence

$$s_1 = \frac{1}{1.000013 \times 0.91674} = 1.09080.$$

For L , Bunsen's experiments (*loc. cit.*) give 80.025. We have, therefore,

$$\frac{dT}{dp} = \frac{1.000116 - 1.09080 \times 273}{4.175 \times 10^7 \times 80.025} = -7.41 \times 10^{-9}.$$

This shows that an increase of pressure of 1 dyne per square centimeter should lower the melting point of ice by 7.41×10^{-9} degree centigrade. Taking 1 megadyne per square centimeter as unit of pressure, the result would be a lowering of temperature equal to 0.00741°C . Sir William Thomson found experimentally that, in two series of experiments in which the pressure was increased from 1 to 8.1 atmospheres, and from 1 to 16.8 respectively (1 atmosphere being equivalent to 1.014 megadyne per square centimeter), the temperature was lowered by 0.0586 and by 0.1289 of a degree. These numbers give

$$0.00725 \text{ and } 0.00757$$

respectively as the lowering of temperature due to a pressure of 1 megadyne per square centimeter, the mean being identical with the calculated number.

Experiments by Mousson in which much greater pressures were employed, whereby the melting point of ice was lowered to -18°C ., are described in the article HEAT (iii. 76).

In the case of substances whose specific volume is greater in the liquid than in the solid state, theory indicates that increase of pressure must raise the melting point, a conclusion which is verified by the results of experiments by Bunsen and by Hopkins, recorded vol. iii. 76.

Changes of Temperature resulting from the Adiabatic Compression of Solids or Liquids.—To find the change of temperature resulting from a given change of pressure

in a solid or liquid, we may start from equation (5b), namely, $dQ = C dt + h dp$. If there is no loss or gain of heat, or $dQ = 0$, and we get, on substituting the value of h from (32),

$$dT = - \frac{T \alpha}{J C \rho} dp. \quad (55)$$

An equivalent expression, giving the change of temperature in terms of the change of volume dv , is obtained by replacing $\frac{dp}{\rho}$ in (55) by $-E dv$, where E is the coefficient of adiabatic elasticity, and then putting for E its value from (35). This gives

$$dT = - \frac{C}{T \alpha \epsilon} \frac{dv}{J \rho} \quad (56)$$

Equation (55) has been verified by Joule (*Phil. Trans.* 1859, 133) by experiments on the effect of pressures suddenly applied to water and to oil. The results, with the data required for comparing them with the calculated values, are given in the following table, where ω denotes the pressure (in megadynes per square centimeter) and θ the rise of temperature (ω and θ here answer to dp and dT respectively in formula (55)). The value of J is taken throughout as 4.175×10^7 .

Thermal Effect of Compression of Water.

T	α	C	ρ	L	θ	
					Experiment	Calculated
273 + 1.2	- 0.000050	1.00006	0.99994	25.69	- 0.0083	- 0.0084
" + 5	+ 0.000016	1.00025	.99999	25.69	+ 0.0044	+ 0.0027
" + 11.69	.000115	1.0006	.99958	25.69	.0205	.0202
" + 18.38	.000193	1.0011	.99858	25.69	.0314	.0346
" + 30	.000300	1.0021	.99577	25.69	.0544	.0561
" + 31.37	.000303	1.0022	.99436	15.86	.0394	.0352
" + 40.4	.000396	1.0035	.99220	15.86	.0450	.0475

With oil the results given in the following table were obtained, showing that the heating effect at a given temperature is proportional to the pressure applied :

T	ω	θ	
		Experiment	Calculated
273 + 16	7.93	+ 0.079	+ 0.089
" + 17.29	15.86	.169	.176
" + 16.27	25.69	.266	.284

In consequence of practical difficulties no experiments have hitherto been made on the thermal effects of the adiabatic compression or extension of solid bodies by stresses acting equally in all directions. The only obvious way of exerting a uniform pressure over the whole surface of a solid is to immerse it in a fluid through which the pressure is transmitted; but when this is done it becomes extremely difficult, if not impossible, to separate the thermal effect due to compression of the fluid from that due to compression of the solid. The changes of temperature produced by the sudden application or removal of forces tending to produce longitudinal extension or compression have, however, been studied in the case of uniform rods or wires, of several materials by Joule (*Phil. Trans.* 1859, 91) and by Edlund (*Pogg. Ann.* 1861, cxiv. 1; 1865, cxxvi. 539). In order that equations (55) and (56) may apply to such cases, we must modify them by introducing M , Young's modulus of elasticity, in place of ϵ , and must take ρ to stand for the mass of unit length of the rod, and α for the coefficient of linear expansion; dv also in the latter formula must be taken as a change of length instead of as a change of volume. It should be noted further that the values of M or ϵ and ρ are certainly, and those of C and α probably, somewhat different, for solid bodies subjected to considerable stress, from the values of the same quantities for bodies not subject to stress: hence a very close agreement between the calculated and experimental results is not to be looked for in the case of such experiments. The following table, taken from Baynes's *Thermodynamics* (p. 162), gives the results of some of Joule's experiments on stretching reduced to absolute measure.

	T	$\frac{1}{\rho}$	α	JO	\mathcal{C}	θ	
						Calculated	Experiment
Iron . . .	273 + 13.3	0.429	1.220×10^{-5}	4.728	321.2	-0.102	-0.101
Hard steel . .	" + 1.7	.448	$1.362 \times$	4.255	321.2	- .127	- .162
Cast iron . .	" + 9.3	.525	$1.125 \times$	4.978	324.9	- .109	- .148
Copper . . .	" + 1.2	.377	$1.718 \times$	3.953	317.7	- .140	- .174
Lead . . .	+ 4.8	.076	$2.858 \times$	1.305	80.0	- .036	- .053

In this table \mathcal{C} denotes the elongating stress, or stretching force in megadynes per square centimeter of the cross section of the bars, and θ the change of temperature, which as indicated by the *minus* sign was a cooling effect. Joule also made numerous experiments on the effect of longitudinal compression upon metal rods. In these experiments a rise of temperature was observed, the results agreeing on the whole well with those calculated by equation (56) when modified in the way already pointed out, to make it suit the case of longitudinal stress.

Escape of Liquids from under Pressure.—If a liquid is forced by a piston through a narrow channel offering so much resistance to its passage that the liquid escapes with a negligible velocity, the temperature of the liquid is raised. This phenomenon was made by Hirn the basis of a method of determining the value of the mechanical equivalent of heat (vi. 686, 687). If the piston exerts a constant pressure p_1 per unit of surface, the work done by the piston in forcing through the channel unit-volume of a liquid is p_1 . Similarly, if p_2 is the pressure (say, that of the atmosphere) which tends to prevent the escape of the liquid, the work done against this, during the passage of as much liquid as occupies unit-volume while under the greater pressure, is $p_2(1 + \alpha \theta' + \frac{1}{E} \varpi)$, if α is the coefficient of expansion, E the coefficient of adiabatic

elasticity, θ' the observed rise of temperature of the liquid, and $\varpi = p_1 - p_2$ the decrease of pressure. This last amount of work added to the mechanical equivalent of the heat produced must be equal to the work done by the first piston. Now the heat developed in the process may be written $C\rho\theta$, if ρ is the density, or mass of unit-volume, of the liquid while under the pressure p_1 , θ the true rise of temperature, and C the specific heat. Hence we have the equation,

$$JC\rho\theta = p_1 - p_2 \left(1 + \alpha\theta' + \frac{1}{E}\varpi\right) = \varpi + p_2\left(\frac{\varpi}{E} + \alpha\theta'\right).$$

Hirn, treating θ and θ' as identical, and neglecting the last term, calculates the value of the mechanical equivalent as

$$J' = \frac{\varpi}{C\rho\theta'}$$

or, since he also takes $C\rho$ for water, the liquid experimented upon, as equal to unity, his formula becomes simply $J' = \frac{\varpi}{\theta'}$. The most important omission in this mode of

treating the result is that which consists in taking θ' , the observed heating effect, as the whole heating effect. According to the last section, a diminution of pressure must lower the temperature of water at any point above its temperature of maximum density, so that the total evolution of heat in Hirn's experiment must have been sufficient to neutralise the cooling due to decrease of pressure as well as to cause the observed rise of temperature. Neglecting, with Hirn, the small term $p_2\left(\frac{\varpi}{E} + \alpha\theta'\right)$ representing external work done by the escaping liquid, we have by the last section

$$J = \frac{\varpi}{C\rho\left(\theta' + \frac{T\alpha\varpi}{JC\rho}\right)} = \frac{\varpi(1 - T\alpha)}{C\rho\theta'} = J'(1 - T\alpha)$$

if J' be taken as the approximate result calculated by Hirn's formula, and if $C\rho$ be put = 1, as is very nearly true for water. Hirn does not give the temperature of the water in his experiments, but only the observed change of temperature θ' . Consequently we cannot calculate the necessary correction, but assuming, for the sake of getting an idea of the possible magnitude of this correction, that the temperature of the water was 10°C. , we have α about = 0.000085, and therefore

$$J = J'(1 - \alpha T) = 433 [1 - 0.000085 \times (273 + 10)] \\ = 423.7$$

as the value in meter-grams of 1 gram-degree of heat. Reduced to ergs, this becomes 4.166×10^7 , or about $\frac{1}{3}$ per cent. less than Joule's result, instead of 2 per cent. higher, as appears from the uncorrected value.

Specific Heat of Saturated Vapours.—We have already had occasion to distinguish between the specific heat of the same substance according as it is exposed to constant pressure or kept at the same volume. Another important case to consider is the case of a mixture of two portions of the same substance in different states of aggregation, say liquid and vapour, when the conditions are such that the quantity of matter existing in each state remains unaltered as temperature is changed. The substance is then said to be in a 'saturated' state. The specific heats of solids and liquids in the saturated state probably do not differ much from their specific heats under constant pressure; but, in the case of saturated vapours, the specific heat is often very different from that of the same vapour under constant pressure. The specific heat of a saturated vapour may be thus calculated. Let it be denoted by γ , and let the specific heat of the saturated liquid in contact with it be represented by C . Also let v_1 be the volume of unit-mass of the liquid, and v_2 the volume of unit-mass of the vapour, and put $u = v_2 - v_1$. 1. Suppose unit-mass of liquid at T converted into saturated vapour at this temperature, and the vapour then heated to $T + dT$ while remaining saturated. The heat required for the evaporation of the liquid is L , of which an amount $\frac{p}{J} u$ is spent in doing external work, if p is the pressure of the saturated vapour. The heat needed to raise the temperature of the vapour is γdT , and of this, an amount $\frac{p}{J} dv_2$ does external work. Consequently, the total quantity of heat employed in doing internal work during the conversion of unit-mass of liquid at T into saturated vapour at $T + dT$ is

$$Q = L + \gamma dT - \frac{p}{J} (u + dv_2)$$

2. Next, let the same transformation be effected in a different way. Raise the temperature of the liquid from T to $T + dT$, and then convert unit-mass into saturated vapour at the higher temperature. The heat needed to raise the temperature of unit-mass is $C dT$, of which an amount $\frac{p}{J} dv_1$ does external work. The heat needed for the evaporation is $L + dL$, and of this a quantity $\frac{p + dp}{J} (u + du)$ is spent in external work. Hence the total quantity employed in doing internal work in this second case is

$$Q' = C dT + L + dL - \frac{p}{J} dv_1 - \frac{p + dp}{J} (u + du).$$

But since in each case a gram of liquid at T has been converted into a gram of saturated vapour at $T + dT$, the expenditure of heat in internal work must be the same in both cases, or $Q = Q'$. Also we have $u = v_2 - v_1$ and $du = dv_2 - dv_1$. Consequently we get for the specific heat of the saturated vapour

$$\gamma = C + \frac{dL}{dT} - \frac{u}{J} \frac{dp}{dT}$$

by (52)

$$= C + \frac{dL}{dT} - \frac{L}{T} \quad (57)$$

We may get numerical results in the case of water-vapour as follows: Taking the specific heat of water under the pressure of saturated vapour as the same as the specific heat under constant pressure, we have, according to Münchhausen (Wüllner's *Compendium der Physik*, ii. 166):

$$C = C_s = 1 + 0.000302 (T - 273)$$

$$= 0.9176 + 0.000302 T$$

$$L = 607.2 - 0.718 (T - 273) \text{ (see Wüllner, } op. cit. \text{ ii. 212)}$$

$$= 803.0 - 0.718 T$$

$$\frac{dL}{dT} = -0.718$$

$$\text{therefore } \gamma = 0.9176 + 0.000302 T - \frac{803}{T}.$$

This expression gives the subjoined numbers for the values of γ at the following temperatures—namely,

Temperature from absolute zero	300°	400°	700°	710°	800°
" zero centigrade	27	127	427	437	527
γ	-1.669	-0.969	-0.081	0	+0.1554

Thus it appears that, below about 437° C., the specific heat of water-vapour is negative: that is to say, heat must be *taken from* it to keep it saturated as the temperature is raised. The physical interpretation of this, at first sight, rather contradictory result is, that a given quantity of water can evaporate completely in a smaller and smaller space as temperature rises; hence, to keep water-vapour saturated when its temperature is raised, it must be compressed into a smaller bulk, and the work done upon it by the compressing force is more than equivalent to the quantity of heat needed to cause the rise of temperature. This result was discovered independently and almost at the same time by Clausius and by Rankine in 1850.

[For a more complete treatment of the subject of Thermodynamics, readers may be referred to the following, among other works:—Rankine, *The Steam-Engine and other Prime Movers*; Clausius, *Mechanische Wärmetheorie* (or English translation by W. R. Browne); Vordet, *Théorie mécanique de la chaleur*; P. de Saint-Robert, *Principes de Thermodynamique*; Rühlmann, *Handbuch der mechanischen Wärmetheorie* (valuable for the completeness with which numerical data are given); Willner, *Die Lehre von der Wärme* (forms the third vol. of this author's *Lehrb. d. Experimental Physik*); Jamin a. Bouty, *Cours de Physique* (tome ii. fascicule 2); Maxwell, *Theory of Heat*; R. E. Baynes, *Lessons on Thermodynamics* (an excellent and comprehensive work in small compass). Most of the above works have been consulted more or less during the compilation of the foregoing article, but use has been chiefly made of Jamin and Bouty and of Baynes.]

G. C. F.

THERMONEUTRALITY. See HEAT (p. 985).

THETINES. This name is given to a series of sulphur-compounds analogous to betaine and its homologues, and represented by the general formula

$$\begin{array}{c} \text{CH}_2-\text{S}(\text{C}^n\text{H}^{2n+1})_2 \\ | \\ \text{CO}-\text{O} \end{array}$$

Only the methyl and ethyl terms are however at present known. See METHYL-THETINE (p. 1317).

THEVETOSIN. A glucoside obtained from the seeds of *Thevetia Yccali* D. C., a tree growing in Mexico, and there called *Joyote*. It crystallises in four-sided prisms, dissolves easily in alcohol, and is resolved by dilute sulphuric acid into glucose and a resinous body. It is very poisonous, acting as an emetic. The seeds also contain a non-drying oil, albuminoids, and extractive matters (Herrera, *Pharm. J. Trans.* [3], vii. 854).

THIACETAMIDE and THIACETANILIDE. See THIAMIDES.

THIACETIC ANHYDRIDE, or *Diacetyl Sulphide*, $(\text{C}^2\text{H}^3\text{O})_2\text{S}$. Barium dioxide acts violently on this compound in the dry state, producing incandescence; but if the anhydride be diluted with ether, the action begins after some time only, and is attended with only slight evolution of heat, the product being acetyl persulphide, $(\text{C}^2\text{H}^3\text{O})_2\text{S}^2$, probably formed according to the equation, $2(\text{C}^2\text{H}^3\text{O})_2\text{S} + \text{BaO}^2 = (\text{C}^2\text{H}^3\text{O})_2\text{S}^2 + (\text{C}^2\text{H}^3\text{O}^2)^2\text{Ba}$ (Beckmann, *J. pr. Chem.* [2], xvii. 439).

THIACETIC ETHERS. *Action of Permanganates.*—Thiethylic ether, or Acetyl-ethyl sulphide, $\text{C}^2\text{H}^3\text{O} \cdot \text{S} \cdot \text{C}^2\text{H}^5$, is but slightly attacked by potassium permanganate; but silver permanganate, even in very dilute solution, is quickly decolorised by it, with formation of acetic and ethylsulphonic acids. Isopentyl thiobenzoate, or benzoyl-isopentyl sulphide, $\text{C}^7\text{H}^9\text{O} \cdot \text{S} \cdot \text{C}^5\text{H}^{11}$, is but slightly attacked by the permanganates of potassium and silver, even at the heat of the water-bath. Ethyl thiobenzoate; on the other hand, is converted by silver permanganate in presence of sulphuric acid, even at ordinary temperatures, into benzoic and ethylsulphonic acids.

THIALDEHYDE, $\text{C}^2\text{H}^4\text{S}$. This compound is known only in polymeric modifications (H. Klinger, *Ber.* ix. 1893; xi. 1023). The oily liquid formed by passing hydrogen sulphide into aldehyde has, according to Pinner, the composition $\text{C}^2\text{H}^4\text{O} \cdot \text{C}^2\text{H}^4\text{S}$, and when treated with acids, yields a precipitate of trithialdehyde or parathialdehyde, $\text{C}^6\text{H}^{12}\text{S}_3$, which compound may also be obtained directly by passing hydrogen sulphide into a strongly acidulated solution of aldehyde (vii. 37). Parathialdehyde thus obtained crystallises in white glistening needles, soluble in alcohol and ether; it begins to sublime at 45°, and may be volatilised without alteration. On adding silver nitrate to its solution in strong alcohol a crystalline compound is formed having the composition $\text{C}^6\text{H}^{12}\text{S}_3 \cdot 2\text{AgNO}_3$.

With *chlorine* or *bromine* it forms chloride or bromide of sulphur, and chloride or bromide of ethylidene, together with more highly chlorinated or brominated products (Pinner, *Liebigs Annalen*, clxxx. 21). By oxidation with potassium permanganate, it yields potassium acetate, sulphuric acid, and potassium ethylenedisulphonate, $\text{CH}^3\text{CH}(\text{SO}^2\text{OK})^2$ (Guareschi, *Gazz. chim. ital.* 1879, 75).

When this parathialdehyde is heated on the water-bath with *acetic* or *benzoic chloride*, it is converted into a new modification (distinguished by Klinger as β -parathialdehyde) which has the same composition and vapour-density as that above described, and likewise crystallises in glistening needles, but melts at 125° , and boils with very slight decomposition at 245° – 248° . With silver nitrate, it forms two crystalline compounds, viz. $\text{C}^6\text{H}^{12}\text{S}_4\text{AgNO}_3$ (compact colourless needles) and $\text{C}^6\text{H}^{12}\text{S}_4\text{AgNO}_3$ (thin nacreous laminæ), which dissolve sparingly in boiling alcohol and detonate when heated.

A third modification, α -parathialdehyde, is produced by subjecting the compound $\text{C}^2\text{H}^4\text{O}, \text{C}^2\text{H}^4\text{S}$, suspended in water, and frequently agitated, to the prolonged action of hydrogen sulphide. An oil is thereby obtained which yields only traces of ordinary parathialdehyde when treated with dilute acids, but on dissolving it in ether, drying the solution over calcium chloride, distilling off the portion which volatilises below 140° , and mixing the residue with a small portion of aldehyde, α -parathialdehyde is obtained. This modification crystallises from alcohol or glacial acetic acid in prisms, melts at 101° , boils between 246° and 247° , and forms with silver nitrate the compounds $\text{C}^6\text{H}^{12}\text{S}_4\text{AgNO}_3$ (concentric groups of dull white needles) and $\text{C}^6\text{H}^{12}\text{S}_4\text{AgNO}_3$ (microscopic prisms), both of which are permanent in the air, and are decomposed by alcohol only after prolonged boiling.

α -Parathialdehyde is converted by acetyl chloride into the β -modification, and the latter is also produced, instead of the α -modification, when the oil obtained as above mentioned for the preparation of the latter by means of hydrogen sulphide, is dissolved in strong sulphuric acid, and the solution is mixed with water, the β -modification then separating out. Both modifications may be crystallised from aldehyde without alteration, and yield the same products by oxidation with dilute nitric acid, viz. acetic acid, aldehyde, carbon dioxide, oxalic acid, sulphuric acid, and sulphur. When exposed to the vapours of fuming nitric acid, they yield sulphonic acids, in addition to the products just mentioned. They are but slowly oxidised by strong nitric acid.

The oil, formed as above described from the compound $\text{C}^2\text{H}^4\text{O}, \text{C}^2\text{H}^4\text{S}$, is converted by ethyl iodide into triethylsulphine iodide, $(\text{C}^2\text{H}^5)^3\text{SI}$.

THIALDINE, $\text{C}^6\text{H}^{12}\text{NS}^2 = \text{CH}^3\text{OH} \begin{smallmatrix} \text{S.CH}(\text{CH}^3) \\ \text{S.CH}(\text{CH}^3) \end{smallmatrix} \text{NH}$ (v. 772). By oxidation in dilute solution with potassium permanganate, this base is converted into sulphuric, acetic, and syrupy ethylenedisulphonic acid, $\text{CH}^3\text{CH}(\text{SO}^2\text{H})^2$ (Guareschi, *Gazz. chim. ital.* 1879, 75).

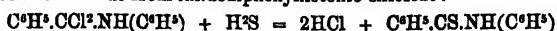
THIAMIDES (Hofmann, *Ber.* xi. 338; Berntsen, *ibid.* 503). These bodies may be conveniently prepared by the action of phosphorus sulphide (? penta-) on amides. When *formanilide*, $\text{H.CO.NH}(\text{C}^6\text{H}^5)$ (5 pts.), is triturated with phosphorus sulphide (3 pts.), the mixture heated for five to ten minutes on the water-bath, and then exhausted with dilute soda-ley, the filtrate, on acidulation with hydrochloric acid, immediately deposits white crystals of *thioformanilide*, $\text{H.CS.NH}(\text{C}^6\text{H}^5)$. Anilino formate may also be used in the preparation instead of formanilide, but it is less advantageous. In like manner, *thiacetanilide*, $\text{CH}^3\text{CS.NH}(\text{C}^6\text{H}^5)$, may be prepared from acetanilide. *Thioformamide*, H.CS.NH_2 , appears to be produced by the action of phosphorus sulphide on formamide. *Thiobenzanilide*, or *Benzothianilide*, is obtained in like manner, in very considerable quantity, from benzanilide (2 pts.) and phosphorus sulphide (1 pt.); and *Phenylthiacetamide* or *Thio-atolylamide*, $\text{C}^6\text{H}^5\text{CH}^2\text{CS.NH}_2$, from phenylacetamide (3 pts.) and phosphorus sulphide (2 pts.).

Thiamides of fatty acids, $\text{C}^n\text{H}^{2n+1}\text{CS.NH}_2$, are also produced by direct addition of hydrogen sulphide to nitrils, e.g. *acetothiamide*, or *thiacetamide*, $\text{CH}^3\text{CS.NH}_2$, from acetonitril, CH^3CN . This compound crystallises, according to Rodewig, in the monoclinic system. Observed faces $\infty P \infty$, $0P$, ∞P , $-P$, sometimes also $+P$; tabular according to $\infty P \infty$. Twins according to $\infty P \infty$. Angle $\infty P : \infty P = 94^\circ 47'$. Axial angle $80^\circ 55'$. The plane of the optic axes is perpendicular to the plane of symmetry. Thiacetamide melts at 108° . It dissolves readily in ether, differing therein from acetamide. Its solution gives with platinum chloride a precipitate of ammonium platinochloride. It is an extremely unstable compound, and is resolved, both by acids and by alkalis into acetic acid, ammonia, and hydrogen sulphide. It is desulphurised by mercuric oxide, iodine solution, silver nitrate, cupric

nitrate, lead acetate, and mercuric nitrate, in some cases immediately, in others only on heating (Bernthsen, *Liebig's Annalen*, xcii. 1).

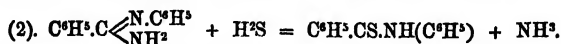
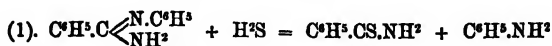
Aromatic Thiamides are produced: 1. From amides, as already mentioned, by the action of phosphorus sulphide.

2. By the action of hydrogen sulphide on imidoketonic chlorides: e.g. thiobenzanilide or benzothianilide from imidodiphenylketonic chloride:

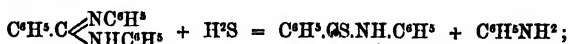


(H. Leo, *Ber.* x. 2133).

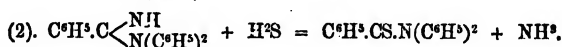
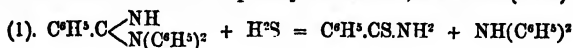
3. By the action of hydrogen sulphide on the amidines of monobasic acids (p. 72). *Benzenylmonophenylamidine* thus treated at 130° yields simultaneously thiobenzamide or benzothiamide (m. p. 115°–116°), and thiobenzanilide (m. p. 95°–97°):



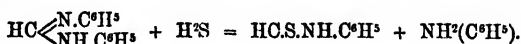
Benzenyldiphenylamidine (m. p. 144°), similarly treated, yields only one compound, viz. thiobenzanilide:



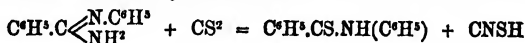
but its isomeride, *benzenyl-isodiphenylamidine* (m. p. 111°–112°), yields two compounds, viz. thiobenzamide and benzodiphenylthiamide, $\text{C}^6\text{H}^5.\text{CS.N}(\text{C}^6\text{H}^5)^2$:



Methenyldiphenylamidine in like manner yields formothianilide or thioformanilide:

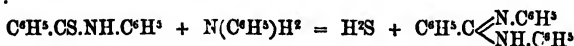


Benzenylmonophenylamidine, heated at 100°–120° with carbon sulphide, yields thiobenzanilide and thiocyanic acid:



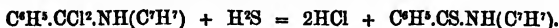
(Bernthsen, *Ber.* x. 1238).

Thiobenzanilide, $\text{C}^{13}\text{H}^{11}\text{NS}$, crystallises in sulphur-yellow tablets melting at 97°. It is not acted upon by iodine. When heated, it gives off hydrogen sulphide, and leaves a body having the composition $\text{C}^{13}\text{H}^{10}\text{N}^2\text{S}^2$. Heated with hydrochloric acid it yields benzoic acid, with evolution of hydrogen sulphide. Heated with potash-ley in a sealed tube at 150°, or with lead oxide, it is converted into benzanilide, $\text{C}^{13}\text{H}^{11}\text{NO}$. Fused with aniline hydrochloride, it yields benzenyldiphenylamidino:



(Leo, *Ber.* x. 2135).

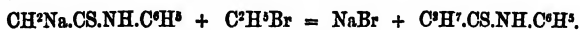
Thiobenzotoluide, or *Benzothiotoluide*, $\text{C}^{14}\text{H}^{13}\text{NS}$, is prepared by the action of hydrogen sulphide on imidotolylphenyl-ketonic chloride:



It melts at 126.5°–129.5°.

Thiacetanilide, $\text{CH}^3.\text{CS.NH}(\text{C}^6\text{H}^5)$, prepared in like manner from imidophenyl-methyl-ketonic chloride, crystallises in light yellow needles melting at 74.5°–76°.

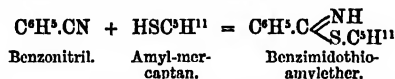
Thiamides containing both fatty and aromatic radicles are formed by the action of haloid ethers (alkyl haloïds) on the sodium-derivatives of aromatic thiamides. Thus sodium-thiacetanilide (which forms compact crystals) and ethyl bromide act upon one another even at temperatures below 100°, forming thiobutyrilanilide, $\text{C}^{10}\text{H}^{11}\text{SN}$:



The best mode of proceeding is to bring together 2 mol. thiacetanilide, 1 mol. sodium and 2 mol. ethyl bromide in alcoholic solution, and, after the action is over and the

alcohol has been expelled, distill off the product in a current of steam. It then passes over as a heavy oil which boils at 250°, is insoluble in water and in alkalis, soluble in alcohol and ether, and is resolved by heating with dilute acids into aniline and a sulphide. Its *hydrochloride*, $C^{10}H^{13}NS.HCl$, prepared by passing hydrogen chloride into the ethereal solution of the base, forms white very soluble crystals; the *platinochloride*, $[C^{10}H^{13}NS.HCl]^2PtCl_4$, is somewhat sparingly soluble. *Methyl iodide* and *sodium-thiacetanilide* yield in like manner a base boiling at 240°. *Ethyl monochloracetate* and *sodium-thiacetanilide* react in a more complex manner, one of the products consisting of ethenyldiphenylamidine, $CH^3.C \begin{smallmatrix} \nwarrow NH.C^6H^5 \\ \nearrow N.C^6H^5 \end{smallmatrix}$ (Wallach, *Ber.* xi. 1590)

Compounds isomeric (or identical) with those thianilides (*imido-thioethers*) are obtained by passing gaseous hydrogen chloride into a mixture of a nitril and a mercaptan in equivalent proportions, the whole then solidifying to a crystalline mass consisting of the hydrochloride of the imido-thioether, e.g.:

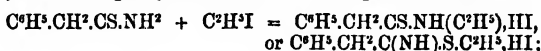


The hydrochloride of this imido-thioether, $C^{12}H^{17}NS.HCl$, crystallises in flat white needles. The free ether is a colourless mobile liquid (Pinner u. Klein, *Ber.* x. 1825).

According to Wallach, the bases obtained by the action of alkyl haloids on the sodium-derivatives of the thiamides are identical in constitution with the imido-thioethers; if so, the formation of one or the other of these bodies must be attended with atomic transposition.

The following thiamides (or imido-thioethers) have been obtained by Bernthsen (*Liebig's Annalen*, cxvii. 341):

Phenylthiacetethylamide, $C^{10}H^{13}NS = C^6H^5.CH^2.CS.NH(C^2H^5)$, or *Phenylacetimidiothioethyl ether*, $C^6H^5.CH^2.C \begin{smallmatrix} \nwarrow NH \\ \nearrow S.C^2H^5 \end{smallmatrix}$, is formed, as a hydriodide, by the action of ethyl iodide on phenylthiacetamide at a temperature below 100°:



and on treating the hydriodide with soda-ley, the thiamide $C^{10}H^{13}NS$ is obtained as an oily body, very unstable, and resolved by heat into mercaptan, C^2H^5SH , and benzylcyanide, $C^6H^5.CH^2.CN$.

Thiobenzethylamide, $C^8H^{11}NS = C^6H^5.CS.NH(C^2H^5)$, or *Benzimidiothioethylether*, $C^6H^5.C(NH).S.C^2H^5$, is obtained, as a crystalline hydriodide, by the action of ethyl iodide on thiobenzamide, $C^6H^5.CS.NH^2$. It resembles the preceding compound, but is much more stable. It is resolved by heat into benzonitril and mercaptan.

Thiobenzo-benzylamide, $C^8H^9.CS.NH(C^2H^5)$, or *Benzimidiothiobenzylether*, $C^6H^5.C(NH).S.C^2H^5$, is obtained as a hydrochloride by heating thiobenzamide with benzyl chloride, or a mixture of benzonitril and benzyl mercaptan with gaseous hydrogen chloride.

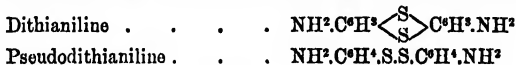
Phenylthiacetamide, *Phenylacetothiamide*, or *Thio-α-tolylamide*, $C^8H^9NS = C^6H^5.CH^2.CS.NH^2$, is obtained by the action of phosphorus sulphide (2 pts.) on phenylacetamide (3 pts.) (Bernthsen); also, together with phenylacetydiamine thio-sulphate, $C^6H^5.N^2S^2O^2$, by the action of hydrogen sulphide on benzyl cyanide (Bernthsen, *Ber.* viii. 677). It unites directly with methyl iodide and ethyl bromide, forming crystallisable compounds which may be regarded as hydriodide and hydrobromide respectively, inasmuch as when placed in water they dissolve at the first instant, forming solutions which immediately give precipitates with silver nitrate; after ten to thirty seconds, however, these solutions become turbid, and deposit fetid oils. When the freshly prepared solution of the product obtained with methyl iodide (which has the composition $C^8H^9NS.CH^3S$, and melts at 138°–139°), is treated with recently precipitated silver chloride, the latter is immediately converted into iodide, and the filtrate gives with platinic chloride fine yellow laminae of the compound $(C^8H^9NSCl)^2PtCl_4$. Phenylthiacetamide and *benzaldehyde*, heated together for three or four hours, unite, with elimination of water, forming a thick yellowish-red oil, $C^{12}H^{22}N^2S^2 = C^6H^5.CH(NH.CS.CH^2.C^6H^5)^2$?, the dilute alcoholic solution of which gives, with platinic chloride, a brown pulverulent precipitate having the composition $C^{12}H^{22}N^2S^2.PtCl_4$ (Bernthsen).

THIAMMELINE, C^8H^9NS , is formed, together with thiomelanuric acid, by the action of ammonia at 100° on perthiocyanic acid. It is a white sandy powder which, when heated with potash, splits up into ammonia and a mixture of cyanic and thio-

cyanic acids. It dissolves in 145 pts. of boiling water. By hot concentrated hydrochloric acid, it is resolved into hydrogen sulphide, ammonium chloride, and cyanuric acid. Nitric acid oxidises it to ammeline nitrate. Heated with ammonia it yields a body having the properties of melamine. Thiammeline dissolves in acids and in alkalis, and gives precipitates with salts of the heavy metals (Ponomareff, *Compt. rend.* lxxx. 1384).

THIANILINE, or **THIOANILINE**, $C^{12}H^{12}N^2S = (C^6H^4.NH^2)^2S$. This compound, which Merz a. Weith obtained by boiling aniline with sulphur (vii. 1154), is also produced: α . By reduction of nitrophenyl sulphide, $(C^6H^4.NO^2)^2S$ (p. 1546). β . By the action of sulphur iodide [$? S^{12}I^2$] on aniline at 160° – 170° , in small quantity however, and mixed with a large amount of resinous products. The thianiline obtained by both these processes melts at 105° – 106° , agreeing therein closely with Merz a. Weith's product, which melted at 104° – 105° . With aniline and sulphur chloride a product was obtained melting at 108° – 109° , and agreeing in all other respects with the preceding (E. Schmidt, *Ber.* ix. 1050; xi. 1168).^{*} Thianiline is also found in the mother-liquor obtained in the preparation of α -triphenylguanidine by the action of thiocarbonyl chloride in ethereal solution on aniline (Rathke, *Liebig's Annalen*, clxvii. 211).

Dithianiline, $C^{12}H^{10}N^2S^2 = (C^6H^3)^2S^2(NH^2)^2$ (E. B. Schmidt, *Ber.* xi. 1168).—This compound is formed, together with monothianiline and resinous sulphuretted products, by the action of sulphur bromide on aniline. Its sulphate is obtained by heating dithiacetanilide (*infra*) with dilute sulphuric acid, and when purified by recrystallisation from water, forms small white slender needles or warty masses which acquire a reddish tint on exposure to the air. It contains 2 mol. water of crystallisation. Dithiacetanilide heated with hydrochloric acid yields, not the corresponding hydrochloride of dithianiline, but a free bisulphuretted base, $C^{12}H^{12}N^2S^2$, designated by Schmidt as *pseudodithianiline*. This base crystallises from water in long thin greenish needles having a vitreous lustre; it melts at 79° , dissolves readily in alcohol, ether, and chloroform, sparingly in benzene, ligroin, and carbon bisulphide. Schmidt represents the two so-called dithianilines by the following formulæ:



Dithiacetanilide, $(C^6H^4.NH.C^2H^3O)^2S^2$, and **Trithiacetanilide**, $(C^6H^4.NH.C^2H^3O)^2S^3$, are formed by the action of sulphur chloride on acetanilide at 100° , and are separated by their different degrees of solubility in glacial acetic acid. **Dithiacetanilide** is easily soluble in glacial acetic acid and in alcohol, and crystallises from the former in large greyish-white laminae, from the latter in pointed shining needles; in other solvents it is either insoluble or very sparingly soluble. It melts at 215° – 217° . By sulphuric or hydrochloric acid it is resolved into acetic acid and dithianiline.

Trithiacetanilide is but sparingly soluble in glacial acetic acid, and crystallises therefrom in nacreous laminae melting at 213° – 214.5° . It is moderately soluble in warm alcohol, from which it separates in stellate groups of small crystals. It is decomposed by sulphuric or hydrochloric acid into acetic acid and trithianiline (Schmidt).

THIOBENZALDEHYDE, $C^6H^5.CHS$ (H. Klinger, *Ber.* ix. 1893; x. 1877). This compound is formed by passing hydrogen sulphide into an alcoholic solution of bitter almond oil, and is obtained, according to the concentration of the solution, either in amorphous reddish flocks, or as a quickly solidifying oil (α -modification). It softens at 83° – 85° , decomposes at a higher temperature, dissolves very readily in benzene and in chloroform, somewhat slowly in hot alcohol. By treatment with acid chlorides, it is converted into a modification (β) which forms white shining needles, melting with decomposition at 225° – 226° , easily soluble in hot glacial acetic acid, less easily in alcohol, benzene, and chloroform. The amorphous modification, heated with finely divided copper, yields $C^{12}H^{12}$.

On adding a very small quantity of iodine to a solution of the amorphous (α) thiobenzaldehyde in benzene, crystalline needles separate in a short time consisting of a compound of β -thiobenzaldehyde (m. p. 225°), with benzene, $C^6H^5.CHS.C^6H^6$, which gives off the benzene at 125° – 130° . 36 pts. of α -thiobenzaldehyde thus treated yield 9 pts. of the β -modification. The latter heated with finely-divided copper yields so

^{*} J. Roorda Smit (*Ber.* viii. 1445), by acting on aniline with sulphur chloride, obtained a body which he calls *thianilide*, having the same composition as thianiline, but differing from the latter altogether in its physical properties, being a yellow oil at ordinary temperatures, and boiling at 230° – 240° . Its diacetyl derivative melts at 125° – 126° ; the dibenzoyl-derivative at 160° .

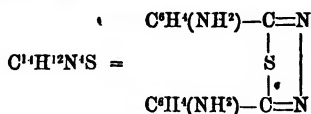
large an amount of stilbene ($\frac{2}{3}$ of its weight) that this method may be advantageously used for the preparation of stilbene (p. 676).

β -Thiobenzaldehyde is converted by oxidation with nitric acid into benzaldehyde and benzoic acid; by heating with lead oxide into lead sulphide and benzaldehyde, together with small quantities of stilbene and high-boiling sulphur-compounds (Klinger). Treated with strong potash-ley it yields a mixture of benzyl hydro-sulphide, benzyl bisulphide, and benzoic acid (Böttiger, *Ber.* xii. 1053).

The thiobenzaldehyde (m. p. 78° – 80°) which Cahours and Fleischer obtained by the action of potassium hydrosulphide on betuzylene chloride, $C^6H^4Cl^2$, in alcoholic solution (vi. 329), is regarded by Klinger as a third modification (γ). It is not converted into the β -modification either by acetyl chloride or by iodine.

THIOBENZAMIDE, $C^6H^5.CS.NH^2$. The action of iodine on this body gives rise, as already mentioned (vi. 258), to the compound $C^{14}H^{12}N^2S$, which crystallises from hot alcohol in long needles melting at 90° .

Amidothiobenzamide, $C^6H^4(NH^2).CS.NH^2$, is acted upon by iodine (both in alcoholic solution) in the same manner, and on evaporating the resulting liquid, there remains a brownish resinous substance, from which, by repeated boiling with water, a body is extracted which separates from the hot filtrate in white slender needles, and when purified by recrystallisation from water has the composition

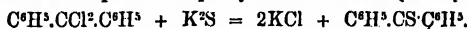


This compound melts between 128° and 129° ; dissolves in alcohol, ether, carbon sulphide, chloroform, and benzene; exhibits marked basic properties; and forms a crystalline sulphate and hydrochloride, also a yellowish bulky platinum salt, with addition of 2 mol. of acid (R. Wanstrat, *Ber.* vi. 332).

THIOBENZANILIDE, $C^6H^5.CS.NH(C^6H^5)$. See **THIAMIDES** (p. 1924).

THIOBENZOIC ETHERS. *Isopentyl* or *Amyl Thiobenzoate*, or *Benzoyl-isopentyl Sulphide*, $C^7H^5O.O.(CH^2)^2CH(CH^3)^2$, is but slightly acted on by the permanganates of potassium and silver even at the heat of the water-bath. The *ethylic ether*, on the other hand, is converted by silver permanganate in presence of sulphuric acid, even at ordinary temperatures, into benzoic and ethylsulphonic acids (Beckmann, *Ber.* xi. 1687).

THIOBENZOPHENONE, or *Diphenyl Thioketone*, $C^6H^5.CS.C^6H^5$, is formed by the action of potassium sulphide on diphenylketonic chloride (benzophenone chloride):



It is also formed as a secondary product in the preparation of thiobenzpinacone (*infra*), and remains in the mother-liquors. It crystallises in small white needles melting at 146.5° , is not attacked in alcoholic solution by copper. By hydrogen sulphide, especially in the nascent state, it is converted in alcoholic solution into thiopinacone (C. Engler, *Ber.* xi. 922).

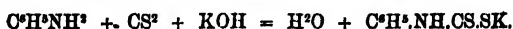
THIOBENZPINAONE, $C^{20}H^{22}S^2 = (C^6H^5)^2(HS)C-C(SH)(C^6H^5)^2$, is formed by the action of ammonium-hydrogen sulphide on benzophenone (Engler, *Ber.* xi. 922); also, together with thiobenzophenone, by the action of potassium-hydrogen sulphide on benzophenone chloride (Behr, *Ber.* vi. 970). It melts at 151° , and is converted in alcoholic solution by finely divided copper into tetraphenylethane, $(C^6H^5)^2HC-CH(C^6H^5)^2$ (p. 1916).

THIOCARBACETO-ACETATE, **ETHYLIC**, $CH^3.CO.C \begin{array}{l} \nearrow CS \\ \searrow COOC^2H^5 \end{array}$.

This ether is formed, together with small quantities of carbon oxide and lead sulphide, when ethylic acetoacetate (p. 12) is heated at 100° in a sealed tube with carbon sulphide and lead oxide, and may be extracted from the product by alcohol. It crystallises in straw-yellow needles, melting at 156° – 162° (Norton a. Oppenheim, *Ber.* x. 701).

THIOCARBAMATES. On the action of Ammonium Thiocarbamate on Aldehydes, see p. 387.

Potassium Phenylthiocarbamate is formed by the action of carbon bisulphide and potassium hydroxide on aniline:



The actual product of the reaction is always however the acid potassium salt, $C^6H^5NS^2K.C^6H^5NS^2$; and this salt is most conveniently prepared by heating an alcoholic solution of aniline and potassium xanthate in molecular proportions for three or four hours, the liquid on cooling first depositing diphenylthiocarbamide and then the acid potassium salt, while a thiocarbamate remains in solution. The acid potassium salt recrystallised from lukewarm water, forms golden-yellow, transparent, monoclinic crystals, which when crushed by pressure, yield a white powder, turning yellowish again at about 30° . Between 60° and 70° the crystals melt in their water of crystallisation; at ordinary temperatures they dissolve in less than their own weight of water. The solution decomposes when heated, yielding diphenylthiocarbamide and phenylthiocarbimide, $C^6H^5.NCS$. The salt when exposed to the air decomposes into phenylthiocarbimide and potassium dithionate, a small quantity of diphenylthiocarbamide being formed at the same time. It is decomposed by salts of heavy metals with formation of phenylthiocarbimide and a metallic sulphide. The potassium salt when heated yields water and diphenylthiocarbamide, and is resolved by acids into aniline and carbon bisulphide. Its solution takes up large quantities of aniline, and if subsequently heated gives off hydrogen sulphide, and deposits diphenylthiocarbamide. The dissolved potassium salt is resolved by *aniline salts* into diphenylthiocarbamide, aniline, carbon bisulphide, and hydrogen sulphide; by *ammonium salts* into diphenylthiocarbamide, ammonia, carbon bisulphide, and ammonium sulphide (B. Rathke, *Ber.* xi. 988).

THIOCARBAMIDE. $NH^2.CS.NH^2$. *Sulphurea* (Berntsen a. Klinger, *Ber.* xi. 492). This body (p. 395) unites with *alcoholic iodides* (alkyl iodides), forming strongly basic compounds, which exhibit the characters of sulphine-compounds. *Methiodide thiocarbamide*, $N^2H^4CS.CH^3I$, crystallises in prisms which melt at 177° , and dissolve readily in water and in alcohol. On agitating its aqueous solution with silver chloride, the iodine is replaced by chlorine. On adding silver oxide to the aqueous solution of the iodide, silver iodide is formed, together with a strong base which has not been isolated: its solution, neutralised with hydrochloric acid and mixed with platinic chloride, yields the *platinochloride*, $(N^2H^4CSCH^3Cl)_2PtCl_4 + H^2O$, which crystallises in groups of small prisms, efflorescing on exposure to the air, and giving off the whole of their water at 110° . The solution of the base gives a characteristic precipitate with metallic salts, and when left to evaporate deposits crystals which after a while cease to exhibit basic reaction. On agitating the aqueous solution of the methiodide-thiocarbamide with *mercuric oxide*, cyanamide, or dicyanodiamide, is produced, together with a yellow flocculent substance resolved by heat into mercuric iodide and methyl sulphide.

The *hydriodide of methylthiocarbamide*, $NH^2.CS.NH(CH^3).HI$, metameric with the compound just described, crystallises in large laminæ, melts below 100° , and yields a platinochloride which crystallises in concentric groups of bent and branched needles. Silver nitrate added to its solution throws down silver iodide and a silver compound of methylthiocarbamide, whereas the solution of the metameric compound, when similarly treated, deposits nothing but silver iodide. The hydriodide of methylthiocarbamide is immediately desulphurised by silver oxide, and converted into methylcyanamide.

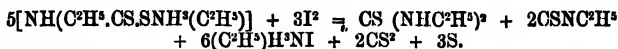
Ethiodide thiocarbamide acts just like the methyl-compound, excepting that when treated with silver oxide it is very easily converted into cyanamide. These addition-products are decomposed when somewhat strongly heated, yielding hydrocyanic acid and products not yet examined, partly amorphous, partly crystalline, the latter being converted into the former by heat.

Thiocarbamide unites also very readily with *benzyl chloride*, forming the compound $CSN^2H^4.C^6H^5Cl$, which may be purified by washing with ether, crystallises from water and from alcohol in small needles, and melts at 166° – 168° . On evaporating its solution in hydrochloric acid, decomposition takes place to a very slight extent, attended with the formation of white bulky needles, while the greater quantity crystallises in large colourless prisms having the same melting point as the crude product. The corresponding *platinochloride* crystallises in yellow prisms. The *free base*, $C^6H^5N^2S$, is separated from the solution of the hydrochloride by ammonia or sodium hydrate in the form of a very bulky white precipitate. It is somewhat sparingly soluble in water, and crystallises from ether, alcohol, or best from benzene, in white felted needles; its solutions decompose very readily when heated, the aqueous solution becoming turbid in consequence of the formation of benzyl hydrosulphide. The base melts at 71° – 72° , and is resolved at a slightly higher temperature into benzyl hydrosulphide and dicyanodiamide. It dissolves readily in acids, the hydrochloride thus formed being identical with that above described (Berntsen a. Klinger, *Ber.* xii. 574).

Thiocarbamide, heated with *thiocarbonyl chloride*, CSCl_2 , yields the hydrochloride of thiodicyanodiamine, $\text{C}^2\text{H}^2\text{N}^2\text{S} \cdot \text{HCl}$ (p. 1930).

On the reaction of thiocarbimide with *ananthyl*, see *ENANTHYLENE THIOCARBIMIDE* (*infra*).

Diethyl-thiocarbamide, $\text{CS}(\text{NHC}^2\text{H}^5)^2$, is formed, together with ethyl thiocarbamide, ethylammonium iodide, carbon bisulphide, and free sulphur, by the action of iodine on ethylthiocarbamate of ethylamine:



Diethylthiocarbamide treated with *iodine* yields sulphur and hydrogen iodide, but no ethylthiocarbimide (Rudneff, *Ber.* xi. 977).

Phenylthiocarbamides.—Mono- and di-phenylthiocarbamide—and likewise phenyl-xanthamide, $\text{C}^6\text{H}^5\text{S} \cdot \text{CO} \cdot \text{NH}^2$ —dissolve in aqueous potash and soda (not in ammonia), and are precipitated from the solution by acids, even by carbonic acid. In these alkaline solutions the two thiocarbamides are easily and completely desulphurised by lead oxide, yielding respectively phenyl cyanamide, $\text{CN}^2\text{H}(\text{C}^6\text{H}^5)$, and diphenylguanidine, $\text{CN}^3\text{H}^2(\text{C}^6\text{H}^5)^2$. The phenylthiocarbamides also dissolve with moderate facility in concentrated hydrochloric acid, the solution of monophenylthiocarbamide being very permanent even at the boiling heat, whereas diphenylthiocarbamide heated with hydrochloric acid is converted into carbanilide, $\text{CO}(\text{NHC}^6\text{H}^5)^2$.

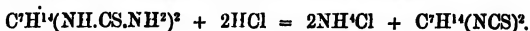
The desulphuration of monophenylthiocarbamide dissolved in alcoholic ammonia produces monophenylguanidine (Rathke a. Feuerlein, *Ber.* xi. 772, 1602).

THIOCARBIMIDES, or **ISOTHIOCYANATES (ALCOHOLIC)**, $\text{R} \cdot \text{N} = \text{CS}$. *Mustard-oils*. *Action of Chlorine and Bromine*. **Ethyl-thiocarbimide**, $\text{C}^2\text{H}^5\text{N} = \text{CS}$ (p. 761), is energetically attacked by dry chlorine, with formation of sulphur chloride and other products of further decomposition; but on passing dry chlorine through a cooled mixture of ethylthiocarbimide and anhydrous ether in equal volumes, the liquid soon solidifies to a thick yellowish pulp, which, when left for a day or two under the air-pump, is converted into an unstable yellowish-white powder. On drenching this powder with soda-ley, a small quantity of sulphur separates, and a heavy brown oil is produced, which after some time solidifies to a crystalline mass; and on pressing this mass between filter paper and dissolving it in a small quantity of alcohol, the solution deposits splendid colourless tablets and prisms, a centimeter long, consisting of a compound of 2 mol. ethylthiocarbimide and 1 at. oxygen, $(\text{C}^2\text{H}^5\text{NCS})^2\text{O}$. The crystals melt at 42° , are insoluble in water, but dissolve easily in alcohol; are oxidised by strong nitric acid, with omission of red fumes; and form with platinum chloride a red non-crystalline compound. On treating their solution with ammonium sulphide, sulphur immediately separates, and the filtrate yields on evaporation fine crystals which melt at about 60° , and therefore do not consist of ethylcarbamide as might have been expected (E. Sell, *Ber.* vi. 322).

On the *Thiocarbimides of Butyl* (primary and secondary), and on *Butenyl- or Crotonyl-thiocarbimide*, $\text{C}^4\text{H}^7\text{NCS}$, see p. 607.

Pentenyl- or Angelyl-thiocarbimide, $\text{C}^5\text{H}^9\text{N} = \text{CS}$, is prepared, like the butyl-compounds, from the volatile mixture of primary and secondary monamines and diamines resulting from the action of ammonia on the dibromide obtained from commercial amylene and bromine. It boils at 190° , and unites directly with ammonia, forming the compound $\text{C}^5\text{H}^9\text{NCS} \cdot \text{NH}^3$, which crystallises in needles and melts at 103° (Hofmann, *Ber.* viii. 105).

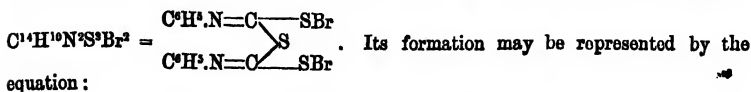
Heptylene- or Enanthylene-thiocarbimide, $\text{C}^7\text{H}^{11}(\text{NCS})^2$. Thiocarbamide and ananthal, dissolved together in alcohol, react on addition of a drop of hydrochloric acid, forming enanthylene-disulphureid, $\text{C}^7\text{H}^{11}(\text{NH} \cdot \text{CS} \cdot \text{NH}^2)^2$; and on mixing the resulting solution with a larger quantity of hydrochloric acid, sal-ammoniac separates out, and enanthylene-thiocarbimide remains dissolved:



Enanthylene-thiocarbimide is an oily liquid having an extremely repulsive odour. By treatment with ammonia, it is reconverted into the above-mentioned *enanthylene-disulphureid*, which forms with ananthal a vitreous polymeride (H. Schiff, *Ber.* xi. 830).

Phenylthiocarbimide, $\text{C}^6\text{H}^5 \cdot \text{N} = \text{CS}$, is converted by *chlorine* into the chloride of phenyl-isocyanide or phenyl-carbamine, $\text{C}^6\text{H}^5\text{N} = \text{CCl}^2$, which is a heavy yellowish liquid having an extremely unpleasant and pungent odour, and boiling at 211° – 212° . *Bromine* acts differently. On mixing phenylthiocarbimide diluted with 3 vol. chloro-

form with an equal weight of bromine, likewise diluted with 3 vol. chloroform, the mixture after a few hours deposits a deep orange-red body having the composition



This orange-red body is decomposed by water at 100° , with evolution of carbon dioxide and hydrogen sulphide, and formation of the hydrobromides of aniline and a base $\text{C}^6\text{H}^5\text{NO}$, which also separates in the free state as a resinous body, and may be obtained by crystallisation from alcohol in long white needles melting at 156° , slightly soluble in hot water, dissolved with difficulty by strong hydrochloric acid, and precipitated from the solution by alkalis. With platinic chloride it forms a well-crystallised double salt.

When the original orange-coloured product is boiled with alcohol, hydrogen bromide and ethyl bromide are evolved, and the liquid on cooling deposits sulphur-yellow crystals of the compound $\text{C}^6\text{H}^5\text{N}^2\text{S}^2 = \text{C}^6\text{H}^5\text{N}=\text{C}-\text{S}-\text{S}-\text{C}=\text{NC}^6\text{H}^5$, while

the base $\text{C}^6\text{H}^5\text{NO}$ remains in the mother-liquor. These crystals, which are also produced by the action of glacial acetic acid on the orange-red body, are insoluble in water, sparingly soluble in cold, easily in hot alcohol, and melt at 152° . When digested for some time in alcohol, they give off hydrogen sulphide and sulphur dioxide; heated at 200° with strong hydrochloric acid, they yield CO^2 , SO^2 , SiH^2 , and aniline. Treated in alcoholic solution with nascent hydrogen, they yield mercaptan, aniline and a resin. Heated with finely divided copper, they are partly converted into phenylthiocarbimide, but at the same time phenyl isocyanide and crystals of unknown composition are formed. When digested with alkaline lead hydroxide, they yield CO^2 , SO^2 , and diphenylcarbamide. The yellow body is not formed by treating phenylthiocarbimide with sulphur, or carbodiphenylimide with sulphur or carbon bisulphide (Proskauer a. Sell, *Ber.* ix. 1262).

Phenylthiocarbimide, treated at ordinary temperatures with hydrogen sulphide, yields thiocarbimide and carbon bisulphide (Proskauer a. Sell).

When vapour of sulphur trioxide is passed over phenylthiocarbimide, sulphur dioxide is given off, and a compound, $\text{C}^6\text{H}^5\text{NS}^2\text{O}^2$, is formed, which dissolves in benzene, and separates therefrom in crystals melting at 180° – 183° . It is insoluble in water, alcohol, ether, and glacial acetic acid, but dissolves in boiling benzene, also in chloroform and nitrobenzene. By water at 100° under pressure, it is resolved into carbon dioxide, hydrogen sulphide, and sulphanilic acid, whence its constitution may probably

be represented by the formula $\text{C}^6\text{H}^5 \begin{array}{c} \text{NH.CS} \\ | \\ \text{SO}^2\text{O} \end{array}$ (Magatti, *Ber.* xi. 2267).

Phenylthiocarbimide and phosphorus pentachloride, heated together in a sealed tube for five or six hours at 160° , form phosphorus trichloride, phosphorus thiocarbimide, PSCl^3 , isocyanphenyl chloride or phenylcarbimide chloride, $\text{C}^6\text{H}^5\text{N}=\text{CCl}^2$, and products of higher boiling point. At the same time there are formed large yellow crystals of the hydrochloride of chlorophenylthiocarbimide, $\text{C}^6\text{H}^5\text{Cl.NCS.HCl}$, which dissolve but sparingly in benzene and chloroform, but readily and with decomposition in water and in alcohol. Water separates chlorophenylthiocarbimide, a strongly refractive oil which may be dried over calcium chloride; it has an aromatic odour, boils at 248° , dissolves readily in alcohol, but is insoluble in water; unites with dry hydrogen chloride, forming a crystalline mass, probably having the composition above specified. According to its chemical reactions, however, this body does not appear to be a true thiocarbimide, not being attacked by alcohol and ammonia even at 100° , and therefore differing from the chlorophenylthiocarbimide previously known.

Water, especially in presence of acids, converts the so-called chlorophenylthiocarbimide at a somewhat higher temperature into the corresponding hydroxyl-compound, $\text{C}^6\text{H}^5\text{NS(OH)}$, which may be conveniently prepared by heating the crude hydrochloride with alcohol till dilute alkalis no longer separate an oil from it. Hydrochloric acid added to the solution throws down the hydroxyl-compound, which quickly solidifies, and may be obtained by solution in hot alcohol, in well-defined crystals melting at 136° . It is insoluble in water and ammonia, soluble in ether and the fixed alkalis, and is precipitated from the latter by acids (A. W. Hofmann, *Ber.* xii. 1126).

The true hydroxyphenylthiocarbimide, $\text{C}^6\text{H}^5\text{(OH).NCS}$, is obtained: a. By boiling

an alcoholic solution of orthamidophenol with carbon bisulphide in a stream of hydrogen:

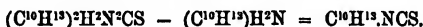


The boiling must be continued as long as hydrogen sulphide continues to escape, and on recrystallising the yellowish-grey crusts thus produced from alcohol and boiling water, the hydroxythiocarbamide is obtained in broad nearly colourless needles melting at 196°. It does not volatilise with vapour of water; chars when heated above its melting point; dissolves readily in ammonia, and crystallises out unaltered. On adding silver nitrate to the ammoniacal solution, white flocks are precipitated which do not blacken when boiled. Boiling aniline decomposes the hydroxyphenylthiocarbamide, with evolution of hydrogen sulphide. Hydrochloric acid at 170° decomposes it into CO², H²S, and amidophenol (J. Dünner, *Ber.* ix. 465).

The same hydroxyphenylthiocarbamide is formed by the action of a high temperature on ortho-hydroxyphenylthiocarbamide, C⁶H⁴(OH).NH.CS.NH² (J. Bendix, *ibid.* xi. 2262).

***o*-Tolyl-thiocarbamide**, C⁶H⁴(CH³)NCS. The action of chlorine on this compound diluted with chloroform, gives rise to a dichloride, C⁶H³NCCL², which boils at 218°, is insoluble in water, and is energetically decomposed by alcohol, glacial acetic acid, and potash-ley. Alcoholic potash converts it into *o*-tolylethyl-urethane, C⁶H³.NH.CO²H³, which melts at 46°, and volatilises with vapour of water, and *o*-ditolyl-carbamide, N²H²(C⁶H³)²CO, which melts at 250°, and does not volatilise with water-vapour (G. Lachmann, *Ber.* xii. 1349).

Cymyl-thiocarbamide, C¹⁰H¹³.NCS (or *Cuminyli-thiocarbamide*), is formed from dicymyl-thiocarbamide by the action of phosphoric anhydride (which abstracts cymyl-amine):

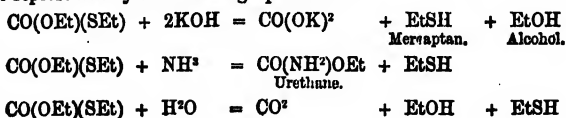


It is a colourless liquid having an odour of mustard-oil, faint at ordinary temperatures, but becoming distinct on heating, and distils, with partial decomposition, between 245° and 270°. It unites after some time with ammonia, forming cymyl-thiocarbamide or cymyl-thiosinamine, (C¹⁰H¹³)H²N²CS, which crystallises in needles, and with cymyl-amine immediately, forming dicymyl-thiocarbamide, (C¹⁰H¹³)²H²N²CS, which crystallises from dilute alcohol in white needles having a satiny lustre, and melting at 128° (A. Raab, *Ber.* x. 52).

THIOCARBONIC ETHERS (F. Salomon, *J. pr. Chem.* [2], vi. 433; vii. 252; viii. 114). Of these ethers, the following are theoretically possible, taking the ethyl-compounds as examples:

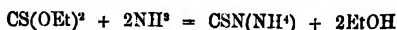
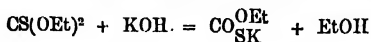
CO ^{SEt} _{OEt}	Carbonyloxythiodiethyl
CS ^{OEt} _{OEt}	Thiocarbonyldioxydiethyl
CO ^{SEt} _{SEt}	Carbonyldithiodiethyl
CS ^{OEt} _{SEt}	Thiocarbonyloxythiodiethyl
CS ^{SEt} _{SEt}	Thiocarbonyldithiodiethyl

1. **Carbonyloxythiodiethyl** is readily obtained by the action of ethyl chlorocarbonate on sodium mercaptide. A mixture of mercaptan with about twice its volume of ether is introduced into a flask surrounded with a freezing mixture, an equivalent quantity of sodium is added, and then ethyl chlorocarbonate by drops. When the reaction is completed, the mass is diluted with about twice its volume of water, and the ethereal layer which rises to the surface is decanted and submitted to fractional distillation. The carbonyloxythiodiethyl then passes over between 150° and 156°. It is a colourless strongly refractive liquid, having an aromatic taste and a peculiar odour like that of rotten fruit. When heated in the air, it burns with a faintly luminous flame, emitting a large quantity of sulphurous acid. It is insoluble in water, but dissolves in alcohol and common ether. Sp. gr. = 1.0285 at 18°. Boiling point 156°. Its reactions with alcoholic potash, alcoholic ammonia, and water are represented by the following equations:

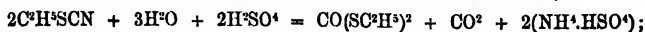


Carbonyloxythiodiethyl is also produced by the action of ethyl bromide on the salt $\text{CO}(\text{OEt})\text{SK}$, produced by the action of alcoholic potash solution on ethyl xanthate, $\text{CS}(\text{OEt})(\text{SEt})$, or by passing carbon oxysulphide, COS , into alcoholic potash.

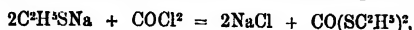
2. *Thiocarbonyl-dioxydiethyl*, $\text{CS}(\text{OEt})^2$.—This ether (*ethylic monosulpho-carbonate*) was discovered by Debus, who obtained it by dry distillation of the compound $(\text{C}^2\text{H}^5\text{O})^2\text{CS}^2$ (v. 497, 499). Salomon finds that it exhibits the properties described by Debus, but is difficult to purify. It exhibits the following reactions:



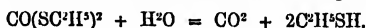
3. *Carbonyl-dithiodiethyl*, $\text{CO}(\text{SEt})^2$, was obtained by the action of strong sulphuric acid on ethyl thiocyanate (Schmitt a. Glutz's method, vi. 413):



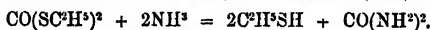
and by that of carbonyl chloride (phosgene) on sodium mercaptide:



the latter method yielding it in theoretical quantity. It is a nearly colourless strongly refracting liquid, easily soluble in alcohol, ether, and strong sulphuric acid. Alcoholic potash decomposes it into carbon dioxide and mercaptan; with alcoholic ammonia it yields carbamide and mercaptan. When heated with water at 160° , or treated with alcoholic potash, it is resolved into carbon dioxide and mercaptan:

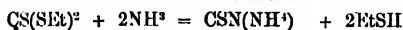
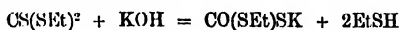


With alcoholic ammonia it yields mercaptan and carbamide (urea):



4. *Carbonyl-oxythiodiethyl*, or *Ethyl Xanthate*, $\text{CS}(\text{OEt})(\text{SEt})$, is best prepared by the action of ethyl bromide on potassium xanthate, the action being then completed in a quarter of an hour, whereas when ethyl chloride is employed (Debus's method) it takes a week.

5. *Thiocarbonyl-dithiodiethyl*, or *Ethyl Trithiocarbonate*, $\text{CS}(\text{SEt})^2$, is also conveniently prepared by the action of bromethyl on the corresponding potassium salt, the action at ordinary temperatures being completed in about twenty minutes. The action of potassium hydroxide and ammonia on this ether is represented by the following equations:



The following table exhibits a comparison of the boiling points of the thiocarbonic ethers above described:

	B. p.	
$\text{CO}^{\text{OC}^2\text{H}^5}_{\text{OC}^2\text{H}^5}$	125°	Diff. 31°
$\text{CO}^{\text{OC}^2\text{H}^5}_{\text{SC}^2\text{H}^5}$	156°	
$\text{CS}^{\text{OC}^2\text{H}^5}_{\text{OC}^2\text{H}^5}$	161°	Diff. 5°
$\text{CO}^{\text{SC}^2\text{H}^5}_{\text{SC}^2\text{H}^5}$	196°	
$\text{CS}^{\text{OC}^2\text{H}^5}_{\text{SC}^2\text{H}^5}$	200°	Diff. 4°
$\text{CS}^{\text{SC}^2\text{H}^5}_{\text{SC}^2\text{H}^5}$	240°	
		Diff. 40°
		Diff. 39°

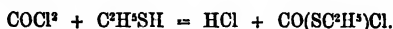
Hence it appears that: 1. The introduction of an atom of sulphur into the ethylated radicle is accompanied by a rise of 40° , except in the case of the first two members of the series, in which the difference is only 31° .

2. The introduction of sulphur into the carbonyl group is attended by a rise of 4° – 5° in the boiling point.

The specific gravities of these isomeric ethers are nearly equal, as shown in the following table, in which they are given for the temperature of 19°:

$\text{CO} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{OC}^2\text{H}^5 \end{smallmatrix} = 0.975$	$\text{CO} \begin{smallmatrix} \text{SC}^2\text{H}^5 \\ \text{SC}^2\text{H}^5 \end{smallmatrix} = 1.085$
$\text{CO} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SC}^2\text{H}^5 \end{smallmatrix} = 1.0285$	$\text{CS} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SC}^2\text{H}^5 \end{smallmatrix} = 1.085$
$\text{CS} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{OC}^2\text{H}^5 \end{smallmatrix} = 1.0325?$	$\text{CS} \begin{smallmatrix} \text{SC}^2\text{H}^5 \\ \text{SC}^2\text{H}^5 \end{smallmatrix} = 1.152$

Carbonyl-thioethyl Chloride, $\text{CO}(\text{SC}^2\text{H}^5)\text{Cl}$, is formed by the action of carbonyl chloride on mercaptan. On saturating mercaptan with the gas and leaving it at rest, the evolution of hydrogen chloride begins after a few hours, and continues till the following day; and the liquid, on subsequent distillation, yields considerable quantities of carbonyl-thioethyl chloride. The formation of this compound is represented by the equation:

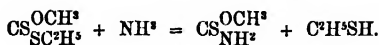


Carbonyl-thioethyl chloride is a colourless strongly refracting liquid, which emits a tear-exciting vapour. It has a density of 1.154 at 16°, and boils at 136°. Treated with *potassium ethylate*, it yields carbonyl-oxythiodiethyl. With aqueous or alcoholic ammonia it forms a crystalline non-sulphuretted body, not yet examined; but when a strong current of gaseous ammonia is passed over the chloride, it solidifies to a crystalline mass, separable by ether into sal-ammoniac, which remains undissolved, and a body which dissolves in the ether and separates therefrom in large dazzling white tablets. This body is thio-ethyl carbamate, $\text{C}^2\text{H}^5\text{NSO} = \text{CO}(\text{SC}^2\text{H}^5)\text{NH}^2$. It is readily soluble in alcohol, ether, and hot water, insoluble in cold water. Heated with potash-ley, it is resolved into carbon dioxide, ammonia, and mercaptan; by prolonged contact with alcoholic ammonia into mercaptan and carbamide.

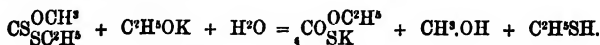
The boiling point of carbonyl-thioethyl chloride (136°) differs from that of carbonyl-oxethyl chloride or ethyl chlorocarbonate, $\text{CO}(\text{OC}^2\text{H}^5)\text{Cl}$ (94°), by nearly the same amount as that which exists between the boiling points of the above-described thiocarbonic ethers and the corresponding carbonic ethers (p. 1961), viz. 42°. The specific gravities of thio- and oxychlorides also differ by the same amount as those of the corresponding thio- and oxycarbonic ethers, viz. by about 0.05 (Salomon, *J. pr. Chem.* [2], vii. 252).

The following methylic and ethyl-methylic thiocarbonates have been prepared by Salomon a. Manitz (*J. pr. Chem.* [2], viii. 114):

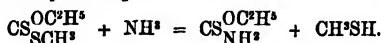
1. *Thiocarbonyl-oxymethylthiethyl*, $\text{CS} \begin{smallmatrix} \text{OCH}^3 \\ \text{SC}^2\text{H}^5 \end{smallmatrix}$, obtained by the action of ethyl iodide on potassium methylxanthate, $\text{CS}(\text{OCH}^3)\text{SK}$, is a liquid closely resembling ordinary xanthic ether in colour and odour, boiling at 184°, and having a density of 1.12 at 18°. With alcoholic potash it is resolved into methylxanthamide (m. p. 45°) and mercaptan:



On adding potassium ethylate (2 vol.) to the ether (1 vol.) diluted with alcohol, the potassium salt, $\text{CO} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SK} \end{smallmatrix}$, separates in slender needles. The decomposition is represented by the following equation:



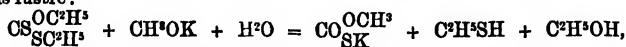
2. The isomeric ether, $\text{CS} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SCH}^3 \end{smallmatrix}$, formed by the action of methyl iodide on potassium ethylxanthate, resembles the preceding in all its physical properties, and is decomposed in the same manner by potassium ethylate, yielding the salt $\text{CO}(\text{OC}^2\text{H}^5)\text{SK}$. By alcoholic ammonia, on the other hand, it is converted into xanthamide, $\text{CS}(\text{OC}^2\text{H}^5)\text{NH}^2$, and methyl mercaptan:



3. *Thiocarbonyl-oxymethyl-thiomethyl*, or *Dimethyl Xanthate*, $\text{CS} \begin{smallmatrix} \text{OCH}^3 \\ \text{SCH}^3 \end{smallmatrix}$, produced by the action of methyl iodide on potassium methylxanthate, is a faintly coloured, somewhat strongly refractive liquid, having a density of 1.176 at 18°

and boiling at 167°–168°. With ammonia it yields methyl-xanthamide, $\text{CS}(\text{OCH}^3)\text{NH}^2$ (m. p. 43°); with potassium ethylate, the ethyl compound $\text{CO}(\text{OC}^2\text{H}^5)\text{SK}$.

The peculiar action of potassium ethylate on these ethers, leading in all cases to the formation of an ethyl-compound as final product, is repeated in the action of potassium methylate on the ethylic ethers $\text{CS}(\text{OC}^2\text{H}^5)(\text{SC}^2\text{H}^5)$ and $\text{CS}(\text{OC}^2\text{H}^5)(\text{SOCH}^3)$, whereby in each case the salt $\text{CO}(\text{OCH}^3)\text{SK}$ is obtained in tufts of needles having a vitreous lustre:

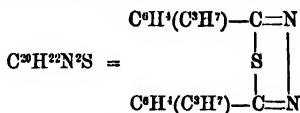


the ethyl in the group OC^2H^5 being replaced by methyl. Hot alcohol also acts in a similar manner, converting the last-mentioned salt $\text{CO} \begin{smallmatrix} \text{OCH}^3 \\ \text{SK} \end{smallmatrix}$ into $\text{CO} \begin{smallmatrix} \text{OC}^2\text{H}^5 \\ \text{SK} \end{smallmatrix}$, whereas with methyl alcohol the reverse action is not produced (Salomon).

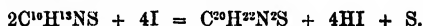
Carbonyl-dithio-dipseudopropyl or *Dithiopseudopropyl Carbonate*, $\text{CO}[\text{SCH}(\text{CH}^3)]_2$, formed by the action of strong sulphuric acid on pseudopropyl mercaptan, is a liquid having a repulsive alliaceous odour, and converted by hydrogen sulphide into *perthiopseudopropylurethane*, $\text{CS}(\text{SC}^2\text{H}^5)\text{NH}^2$, which crystallises from alcohol and ether in laminae having a splendid silky lustre and melting at 97° (Gerlich, *Ber.* viii. 650).

THIOCUMYLAMIDE, or THIOCUMINAMIDE,

$\text{C}^0\text{H}^{11}\text{NS} = \text{C}^0\text{H}^{11}\text{CS.NH}^2$. This compound is acted upon by iodine in the same manner as thiobenzamide (vi. 358). On mixing the two substances in alcoholic solution, decoloration immediately takes place, sulphur is separated, and hydriodic acid is formed; and if the addition of iodine be continued till an excess of it is indicated by addition of starch-solution, and the alcohol be then distilled off, there remains a brownish oil, which, when washed with ammoniacal water, decanted from the latter, and stirred for some time with a glass rod, solidifies to a white amorphous mass, contaminated with sulphur, which is difficult to separate. When freed from this impurity by a somewhat circuitous process, the product is obtained in the form of transparent colourless prisms several lines long, and melting at 45°. It has the composition



and its formation is represented by the equation:



It is insoluble in water, soluble in ether, alcohol, chloroform, carbon sulphide, benzene, and strong sulphuric acid, and is separated from the last-mentioned solvent by water in its original state. By prolonged boiling with strong potash- or soda-ley, it is resolved into sulphur and cumonitril, $\text{C}^0\text{H}^{11}\text{N}$, which latter, by assumption of the elements of water, is converted into ammonia and cumic acid. Thiocumylamide is not attacked by dilute alkalis or by lead oxide (*R. Wanstrat, Ber.* vi. 332).

THIOCYANATES, CN.S.R. See pp. 602–606. On the preparation of Metallic Thiocyanates on the large scale, see Tcherniak a. Günzburg (*Jahresb. f. Chem.* 1878, 1123).

On Alcoholic Isothiocyanates or Thiocarbimides, $\text{CS}=\text{N.R.}$, see pp. 606–608, and 1958–1960.

THIOCYMENE, $\text{C}^{10}\text{H}^{12}\text{SII.}$ See CYMENE-MERCAPTAN (p. 623).

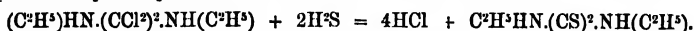
THIODICYANODIAMINE, $\text{C}^2\text{H}^6\text{N}^4\text{S} = \text{NH}^2.\text{CS.NH.C}(\text{NH}).\text{NH}^2$. This compound is formed by the action of thiocarbonyl chloride, CSCl^2 , or of phosphorus pentachloride, on thiocarbamide. The reaction with PCl^5 is represented by the equation:



Thiodicyanodiamine is a base forming transparent monoclinic crystals, which dissolve in water, sparingly in alcohol, and yield a strongly alkaline solution. When heated above 100°, it melts and is completely transformed into the isomeric guanidine thiocyanate, $\text{HN}=\text{C}(\text{NH}^2)_2.\text{HCNS}$.

The *hydrochloride*, $\text{C}^2\text{H}^6\text{N}^4\text{S.HCl}$, forms fine transparent rhombic crystals, which dissolve freely in water and alcohol. The *platinochloride* is an amorphous dark-coloured salt. The *oxalate*, $\text{C}^2\text{H}^6\text{N}^4\text{S.C}^2\text{H}^2\text{O}^4 + \frac{1}{2}\text{H}^2\text{O}$, forms small granular crystals, sparingly soluble in water. Both salts have an acid reaction (*Rathe, Ber.* xi. 962).

THIODIETHYLOXAMIDE, $C^6H^{12}N^2S^2 = (C^2H^5)HN(CS)^2NH(C^2H^5)$ (Wallach a. Pirath, *Ber.* xii. 1063). When diethyloxamide is mixed with phosphorus pentachloride, the mixture first liquefies, and if it be then gently warmed, gives off a large quantity of hydrogen chloride. If now the operation be interrupted at the first stage, and hydrogen sulphide be passed into the well-cooled liquid diluted with benzene, till hydrogen chloride ceases to be given off, thiodiethyloxamide will be formed, and will separate, as the benzene evaporates, in large, reddish-yellow, transparent plates. In the formation of this compound the oxygen of the diethyl-oxamide is first replaced by chlorine, and the resulting amidochloride is then decomposed by the hydrogen sulphide, as represented by the equation:



Thiodiethyloxamide melts at 54° . Treated with sodium ethylate and ethyl bromide it yields an oily liquid, which boils at a temperature above 250° , and probably has the composition $(C^2H^5)N=(CSC^2H^5)^2=N(C^2H^5)$, but it has not been obtained in the pure state.

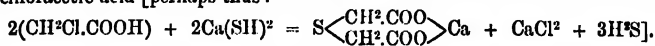
By treating the product of the action of phosphorus pentachloride on *oxanilide* with hydrogen sulphide, a compound is obtained which crystallises from ethereal solution in golden-yellow plates.

THIODIGLYCOLLIC ACID, $C^2H^4SO^4$ (*infra*).

THIOFORMANILIDE, $C^7H^7NS = C^6H^5.NH.CSH$, is produced: 1. By the action of phosphorus pentasulphide on formanilide or aniline formate. 2. By the action of dry hydrogen sulphide on phenyl-carbimide, $C^6H^5.NC + H^2S = C^6H^5.NH.CSH$. 3. Together with large quantities of *m*-methenyldiphenyl-diamine, $C^{12}H^{12}N^2$ (p. 1302), when a saturated alcoholic solution of potassium hydrosulphide is added to a well-cooled alcoholic solution of aniline (1 mol.), chloroform (1 mol.), and potassium hydroxide (3 mol.) The liquid, after standing for a few hours, is mixed with water, the golden-yellow oil thereby separated (consisting of thioformanilide-*m*-methenyldiphenyldiamine, phenylcarbimide, aniline, and chloroform) is treated with hydrochloric acid; and after the chloroform has been evaporated by exposure to the air, the mass, which has now become crystalline, together with the crystals obtained from the mother-liquor of the oil after supersaturation with hydrochloric acid, is recrystallised as quickly as possible from boiling water. The filtered liquid on cooling deposits thioformanilide in thin lamina, while methyldiphenyldiamine hydrate remains in the mother-liquor. The thioformanilide is purified by dissolving it in boiling alcohol, and adding hot water to the solution till it begins to show turbidity. The liquid on cooling deposits the thioformanilide in long white needles which melt at 137.5° , decomposing at the same time into phenylcarbimide and hydrogen sulphide. Its solutions taste intensely bitter. It dissolves without alteration in cold potash-ley, and is precipitated therefrom by acids; but hot potash-ley decomposes it into formic acid, aniline, and hydrogen sulphide (A. W. Hofmann, *Ber.* x. 1095).

THIOGLYCOLLIC ACID, $C^2H^4O^2S = CH^2(SH).COOH$. This acid, already described (p. 884), is one of the products of the action of phosphorus pentachloride on sulphacetic acid (R. Siemens, *Ber.* vi. 659).

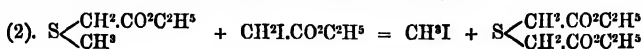
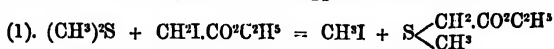
Thiodiglycollic Acid, $C^2H^4SO^4 = S \begin{smallmatrix} CH^2.COOH \\ CH^2.COOH \end{smallmatrix}$ [v . 776]. The calcium salt of this acid is produced by the action of recently prepared calcium sulphhydrate on monochloroacetic acid [perhaps thus:



After the two solutions have been boiled together in a reflux apparatus for eight hours, while a slow stream of hydrogen sulphide is passed through the liquid, the excess of calcium sulphhydrate is decomposed by carbonic acid, the filtrate evaporated to the crystallising point, and the separated crystalline mass is freed from calcium chloride by means of hot strong alcohol, and recrystallised from water. The calcium-salt thus obtained, $C^2H^4SO^4Ca$, dissolves in 48.6 pts. water at 21° , somewhat more readily in boiling water. Its solution is not precipitated by barium chloride. With *lead acetate* it gives a white precipitate which dissolves on boiling, and is also soluble in nitric acid; with *silver nitrate* a white precipitate, which is easily soluble in nitric acid and in ammonia, and does not turn perceptibly brown when boiled with water; but on adding a little ammonia to the water, the odour of ammonium sulphide becomes perceptible and silver sulphide is separated. *Mercuric chloride* also gives with the solution of the calcium salt a white precipitate which does not dissolve on boiling. The mother-liquor obtained in the preparation of the calcium salt contains calcium thioglycollate (C. Schreiber, *J. pr. Chem.* [2], xiii. 436).

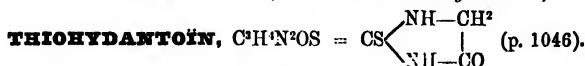
According to Böttiger (*Ber.* xi. 1899), the action of hydrogen sulphide on glyoxylic acid in presence of silver oxide, produces simultaneously thioglycollic and thiodiglycollic acids, which may be separated by converting them into ethylic ethers, and fractionally distilling the product, whereupon one portion passes over at 160° and the other at 260°.

Diethylic Thiodiglycollate, $S(CH^2.CO^2C^2H^5)^2$, is formed by the action of methyl sulphide on ethyl iodacetate, which appears to take place by two stages, thus:



(Letts & Collie, *Edinb. Roy. Soc. Trans.* xxviii. pt. 2, p. 583).

Thiodiglycollamide, $S[CHNH^2.COOH]^2$, crystallises in acute square pyramids with very distinct basal cleavage (Arzruni, *Zeitschr. Kryst.* i. 447).

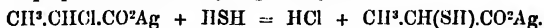


Nitrosothiohydantoin, $C^3H^4(NO)N^2OS$, may be prepared by treating thiohydantoin with nitric acid of sp. gr. 1.2, or by passing nitrous gas through a mixture of thiohydantoin and water. It separates out as a crystalline powder, and may be obtained in microscopic pyramids by recrystallisation from a large quantity of boiling water. It is soluble in alkalis, but insoluble in alcohol, ether, carbon sulphide, and hydrocarbons. With 1 equiv. of an alkali it yields a red solution, but if 2 equiv. of alkali are used, a yellow solution is formed which turns red on addition of an acid.

When *barium chloride* is added to a solution of nitrosothiohydantoin in ammonia, glistening yellow hexagonal and rhombic plates separate out, having the composition $C^3H^4(NO)N^2OS, BaH^2O^2, H^2O$. This compound is but very slightly soluble in cold water, and is partly decomposed by recrystallisation from hot water. On the addition of an acid it yields a red barium-compound, which is soluble in water, but has not been obtained in the pure state. The red solution gives a yellowish-red precipitate with lead acetate, orange-coloured with zinc chloride and mercuric chloride, dark-red with silver nitrate. On adding silver nitrate to an ammoniacal solution of nitrosohydantoin slightly acidulated with acetic acid, the compound $C^3H^4(NO)AgN^2OS, Ag^2O$ separates as a dark reddish-brown precipitate. A similar compound is formed with ferrous salts (R. Maly, *Ber.* xii. 967).

THIOHYDROBENZOIC ACID. Syn. with THIOBENZOIC ACID, $C^6H^4(SH).COOH$. See BENZOIC ACIDS (p. 297).

THIOLACTIC ACID, $C^3H^4SO^2 = C^3H^4(SH).COOH$ (C. Böttiger, *Ber.* ix. 404, 804, and 1061; xi. 1561). This acid is formed: 1. By decomposing the silver salt of α -chloropropionic acid with hydrogen sulphide:



This reaction determines the constitution of the acid.

2. By similar treatment of silver pyroracemate. The pyroracemate suspended in water is decomposed by hydrogen sulphide, and the liquid, when saturated with the gas, is left to itself for a week, then filtered, and the filtrate is concentrated by distillation. Acetic acid then passes over, and the remaining liquid, freed from precipitated silver and silver sulphide, is repeatedly agitated with ether. The oily ether-residue spread out in a thin layer, changes in the course of a fortnight into a crystalline crust of thiolactic acid, greasy to the touch, which may be purified by repeated crystallisation.

Thiolactic acid crystallises from aqueous solution in groups of transparent rectangular plates. It dissolves with extraordinary facility in hot water, much less easily in cold water, very sparingly in dilute sulphuric acid, and crystallises therefrom in prismatic needles melting at 141°. These properties, however, are considerably modified by the smallest quantities of impurities, the melting point even by the presence of moisture. The solution of the acid nearly neutralised with ammonia gives with *lead acetate* and *mercuric chloride* precipitates which are quite insoluble in water, but soluble in acids; the dilute solution of the free acid gives a similar precipitate with *mercury nitrate*; with *lead acetate* and *mercuric chloride* it gives either no precipitate, or precipitates which after a while are redissolved. When the acid is oxidised by dilute *chromic acid*, a small quantity of sulphur is precipitated on gentle heating, and on boiling the liquid, sulphuric, acetic, and carbonic acids are formed.

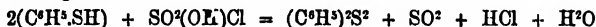
When hydrogen sulphide is passed into pure pyroracemic acid, a compound of

lactic and thiolactic acids is produced, and in such quantity that the whole solidifies to a thick white pulp. This compound, when washed with ether and dried in the exsiccator, has the composition $C^6H^8SO^3 = C^3H^4O^3 + C^3H^4SO^2$. It begins to melt at 87° , decomposing at the same time, the portion which remains solid being somewhat sparingly soluble in cold water. The compound when kept in a tightly-closed bottle is converted within a week into an oil, with evolution of hydrogen sulphide. If the precipitate formed by hydrogen sulphide in pyroracemic acid be left for some time in contact with the liquid, or if the passage of the gas be prolonged, the precipitate redissolves, being probably converted into thiolactic acid, which however is more readily produced from the solid body by heating with hydriodic acid.

THIONESSAL, C^2H^2S (vi. 1087). This compound is formed, together with others, by the action of heat on benzyl sulphide, and is easily separated from the portion of the product which passes over between 360° and 460° , by fractional distillation, and crystallisation from absolute alcohol of the fraction which distils between 440° and 460° . It forms closely felted groups of white brittle needles, melts at 184° , sublimes in needles without alteration, and boils at about 460° . It dissolves with moderate facility in ether and carbon sulphide, less easily in ligroin, very sparingly in alcohol. Its ethereal solution is not precipitated by bromine, and on evaporating the ether, needle-shaped crystals remain having the original melting point. When treated with chromic acid mixture, it blackens and yields carbonic and benzoic acids. It is not altered by boiling with alcoholic potash (C. Forst, *Liebig's Annalen*, clxxviii. 370).

THIONYL CHLORIDE, $SOCl^2$. Syn. with SULPHUROUS CHLORIDE (vii. 1131).

THIOPHENOL, $C^6H^5.SH$. *Phenyl Hydrosulphide* or *Phenyl-mercaptan* (p. 1546). This compound, treated with *sulphuric hydrozoychloride*, is converted into phenyl disulphide:



(Beckurts a. Otto, *Ber.* xi. 2065).

Treated with *acetyl chloride*, it yields phenyl thiacetate, $C^6H^5.S.C^2H^3O$, a colourless liquid having an intensely mercaptan-like and at the same time ethereal odour, and boiling at 218° – 220° (corr. 227° – 229°). It sinks in water, and is at the same time slowly decomposed thereby, with formation of thiophenol. By boiling with strong potash-ley it is completely resolved into thiophenol and acetic acid. With *benzoyl chloride*, thiophenol forms a compound which crystallises in fine white prisms (Michler, *Ber.* vii. 1312).

THIOPHTHALIC ACIDS, $C^6H^4(COSH)(COOH)$. See PHTHALIC ACIDS (p. 1617).

THIOPRUSSIAMIC ACIDS. This name is given by Claus a. Seippel (*Ber.* vii. 233; *Liebig's Annalen*, clxxix. 184) to certain sulphuretted compounds, which are formed by the action of heat on ammonium thiocyanate, and may be regarded as products of decomposition intermediate between thiocarbamide and melam. The compounds which have been investigated are—a *dithioprussiamic acid*, $(NH^2)C^2Cy^3.NH.Cy^3(SH)^2$, a *monothiodiprussiamic acid*, and a *dithiotripurssiamic acid*, $NH^2Cy^3.NH^2.NH.NH^2Cy^3.NH.SH.Cy^3(SNH^4)$. The first of these acids gives no coloration with ferric chloride, the other two give the thiocyanate reaction. The precipitates formed in their concentrated solutions by *lead acetate* are soluble in boiling water, a property by which these acids are especially distinguished from other thiocyanogen compounds. With dilute hydrochloric or nitric acid all the three acids are resolved, even at ordinary temperatures, into melamine and a sulphuretted body (or several) not yet examined.

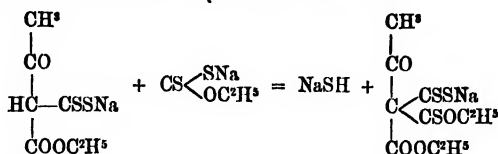
THIOQUINOL, $C^6H^4(SH)^2$ [1 : 4]. This compound is obtained by the action of tin and hydrochloric acid on benzeneparadisulphonic acid (p. 251), in the form of a crystalline sublimate, consisting of shining hexagonal laminæ; it separates also in the same form from boiling alcohol, in which it is slightly soluble. It smells somewhat like tropeolum, and melts at 98° . When exposed to the air it gradually oxidises to a yellow powder. Its lead-compound is an orange-red precipitate (Körner a. Monselise, *Gazz. chim. ital.* 1876, 133).

THIORESORCINOL, $C^6H^4(SH)^2$ [1 : 3], obtained in like manner from benzene-meta-disulphonic acid, exhibits the properties described by Patzschke (vii. 1156). It smells like the leaves of some kinds of geranium, melts at 27° , and boils at 240° (Körner a. Monselise, *loc. cit.*)

THIORUFIC ACID, $C^{10}H^{14}.S^2O^4$ (Norton a. Oppenheim, *Ber.* x. 686). An acid formed by the action of carbon bisulphide on the mixture of sodium ethylate and

ethyl acetosodacetate obtained by treating ethyl acetate with sodium (p. 11). The product, after washing with water, is a light yellow acid substance, nearly insoluble in water, and crystallising in scales having a dark orange-red colour and nacreous lustre. On evaporating its solution in alcohol or acetic ether, it is decomposed. Its *calcium salt*, $(C^{10}H^{13}S^2O^4)^2Ca$, crystallises in cherry-red needles. The *mercury, lead, and zinc salts* are orange-coloured; the *iron salt* brown, the *silver salt* red, the *copper salt* black.

The formation of the acid may be explained by supposing that the acetylated thiomalonic acid and sodium hydrosulphide, which might be expected to form in the first instance, separate out, and that the residues unite, thus:



THIOSULPHURIC ACID. See SULPHUR, ACIDS OF (p. 1879).

THIO- α -TOLYLAMIDE, $C^8H^9NS = C^6H^5 \cdot 3H^2 \cdot CS \cdot NH^2$. See THIAMIDES (p. 1954).

THOMSONITE. This mineral, from the Palle Rabbigge, Monte Monzoni, has been analysed by Doelter & John (*Verh. geol. Reichsanst.* 1875, 295, 304). The needle-shaped crystals analysed were intimately mixed with calcite, to the amount of 19 per cent., after deduction of which their analysis gave:

SiO ²	Al ² O ³	CaO	MgO	NaO	K ² O	H ² O	
39.24	27.90	12.45	trace	7.95	0.60	11.86	100

THORIUM. This metal is not isomorphous with any other known element. A number of its compounds have lately been examined by P. T. Clove (*Bull. Soc. Chim.* 1874, xxi. 116). The atomic weight was found, from the mean of six analyses of the anhydrous sulphate, to be 233.8; from the analyses of the oxalate, 233.97.

Thorium Oxide, or *Thoria*, obtained by ignition of the hydroxide, is insoluble in dilute acids, soluble in warm strong sulphuric acid. When the oxide obtained by ignition of the oxalate is heated with excess of nitric or hydrochloric acid, and the excess of the acid—which does not appear to dissolve or act in any way on the oxide—is expelled by heating on the water-bath, a residue is obtained which dissolves completely in water, the solution appearing white in reflected light, like milk and water or a solution of glycogen, and yielding, on addition of a little acid or salt solution, a curdy precipitate which redissolves in pure water. With ammonia the solution gives a bulky precipitate, which resembles thorium hydroxide, but is insoluble in acids even at the boiling heat. When hydrochloric acid is used for the preparation of the soluble body (in which case a certain quantity of the normal chloride is also produced), the precipitate formed by ammonia has the composition $Th^4O^2(OH)^2$. The normal hydroxide dried at 100° contains $Th(OH)^4$.

Thorium Chloride, $ThCl^4 \cdot 8H^2O$, obtained by decomposing the sulphate with barium chloride, forms white very deliquescent needles. *Thorium-potassium chloride*, $2ThCl^4 \cdot KCl \cdot 18H^2O$, forms colourless crystals easily soluble in water. The *platinichloride* has the composition $ThCl^4 \cdot PtCl^4 \cdot 12H^2O$.

Thorium Silicofluoride, obtained by treating the hydroxide with silicofluoric acid, is a crystalline semi-translucent mass, insoluble in excess of silicofluoric acid; when left over sulphuric acid, it gives off hydrogen fluoride and silicon fluoride.

Thorium Platinocyanide, $ThPt^2Cy^8 \cdot 16H^2O$, crystallises in yellowish-green well-defined orthorhombic prisms, very soluble in hot, sparingly in cold water; gives off $14H^2O$ at 100° or over sulphuric acid. The *ferrocyanide*, $ThFeCy^6 \cdot 4H^2O$, is a white powder. The *thiocyanate* is obtained as a viscid mass by evaporating a solution of thorium hydroxide in thiocyanic acid. Its solution gives with mercuric cyanide an amorphous precipitate consisting of $Th(OH)^2SCy \cdot HgCy^2 \cdot H^2O$, and the filtrate on cooling deposits nacreous scales of the salt $Th(OH)(SCy)^3 \cdot 3HgCy^2 \cdot 12H^2O$.

Thorium Nitrate, $Th(NO^3)^4 \cdot 12H^2O$, forms large, transparent, very hygroscopic tablets, which give off $8H^2O$ over sulphuric acid. The *chlorate* and *perchlorate* are hygroscopic soapy masses. The solution of the *bromate* decomposes when evaporated in a vacuum. The *iodate*, $Th(IO^3)^4$, is a white amorphous precipitate.

Thorium-sodium Carbonate, $Th(CO^3)^2 \cdot 3Na^2CO^3 \cdot 12H^2O$, is a white amorphous precipitate.

Thorium Sulphate, $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$, forms monoclinic crystals very slightly soluble in water, insoluble in alcohol; gives off $7\text{H}_2\text{O}$ over sulphuric acid. Sulphates have also been obtained containing 8 and 3 mol. H_2O . *Thorium-sodium sulphate*, $\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, forms thin needles. *Thorium-ammonium sulphate*, $\text{Th}(\text{SO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4$, prisms soluble in water and in ammonium sulphate. *Thorium sulphite* has the composition $\text{Th}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$.

Thorium Selenate, $\text{Th}(\text{SeO}_4)_2 \cdot 9\text{H}_2\text{O}$, forms bulky crystals permanent in the air, giving off $8\text{H}_2\text{O}$ at 120° . The *selenite*, $\text{Th}(\text{SeO}_3)_2 \cdot \text{H}_2\text{O}$, is a white amorphous precipitate insoluble in water.

Phosphates.—The *orthophosphates*, $\text{ThH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{ThH}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, are bulky precipitates. The *pyrophosphate* has the composition $\text{ThP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. *Thorium-sodium pyrophosphate*, $\text{ThNa}_4(\text{P}_2\text{O}_7)_2$, crystallises with 2 mol. H_2O .

Thorium Formate, $\text{Th}(\text{CHO}_2)_4 \cdot 3\text{H}_2\text{O}$, forms flat well-defined prisms which give off $2\text{H}_2\text{O}$ over sulphuric acid, and $3\text{H}_2\text{O}$ at 100° . The *acetate* forms microscopic needles. The *oxalate*, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, is insoluble in water. *Thorium-sodium oxalate*, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{K}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, is decomposed by water. *Thorium tartrate*, $(\text{C}_4\text{H}_4\text{O}_4)_2\text{Th}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, is a white powder which gives off all its water at 100° . *Thorium-potassium tartrate* has the composition $\text{ThK}_2(\text{C}_4\text{H}_4\text{O}_4)_2$.

THYMOHYDROXYCUMIC ACID, $\text{C}^{10}\text{H}^{12}\text{O}^3$ (L. Barth, *Ber.* xi. 567, 1571).

This acid is formed, together with others, by fusing thymol with potassium hydroxide. On dissolving the melt in water, acidulating with sulphuric acid, extracting with ether, and distilling the residue with water, acetic acid passes over with the steam, and the residue of the distillation deposits on cooling crystals (mixed with a little tar) which, by repeated crystallisation from water, may be resolved, though not completely, into: (1) hydroxyterephthalic acid, very slightly soluble even in hot water; (2) thymohydroxycumic acid, moderately soluble in hot, very sparingly in cold water; and (3), an easily soluble portion, consisting of substances precipitable by lead acetate, together with a small quantity of hydroxybenzoic acid.

Thymohydroxycumic acid, after repeated crystallisation with animal charcoal, forms long, thin, colourless, somewhat fragile needles melting at 143° , or sometimes at 141° ; very soluble in ether, alcohol, chloroform, and benzene; dissolving also in water as above stated. The aqueous solution is not perceptibly coloured by ferric chloride, and gives no precipitate with lead acetate. The normal salts have a slight acid reaction. The *normal sodium salt*, $\text{C}^{10}\text{H}^{11}\text{O}^3\text{Na}$, $2-2\frac{1}{2}\text{H}_2\text{O}$, crystallises in broadly laminar masses, sometimes also in well-formed plates. It is very efflorescent and very soluble in water. The *basic sodium salt*, $\text{C}^{10}\text{H}^{10}\text{O}^3\text{Na}_2$, is a very deliquescent crystalline mass composed of microscopic needles. After drying in a vacuum over sulphuric acid, it still retains $1\frac{1}{2}\text{H}_2\text{O}$. The *barium salt*, $(\text{C}^{10}\text{H}^{10}\text{O}^3)_2\text{Ba}$ (at 130°), is easily soluble in water and separates from its solution, when concentrated, in granulo-crystalline masses, seldom in small prisms. The *cadmium salt*, $(\text{C}^{10}\text{H}^{10}\text{O}^3)_2\text{Cd}$, forms microscopic plates, rarely prisms, and, generally contains 1 mol., sometimes 3 mol., water; it is moderately soluble in alcohol and in ether. The *ethyl ether*, $\text{C}^{10}\text{H}^{11}\text{O}^3 \cdot \text{C}_2\text{H}_5$, prepared with alcohol and gaseous hydrogen chloride, is at first liquid, but subsequently solidifies and then melts at $73^\circ-75^\circ$. From dilute alcohol it separates first in oily drops, afterwards in long prisms.

Thymohydroxycumic acid is not at all or but slightly attacked by strong hydrochloric acid at $200^\circ-250^\circ$, but at 250° further action takes place. The acid heated by itself above 300° partly volatilises undecomposed, and is partly resolved into water and the anhydride $\text{C}^{20}\text{H}^{22}\text{O}^5$, which remains as a mass resembling colophony, and likewise separates in the amorphous state from solution in alcohol. The acid heated with quick lime yields phenolic and anisolic products, but neither propyl-phenol nor methyl-ethyl-phenol. By the further action of melting potash it is converted into hydroxyterephthalic acid, together with an easily soluble acid which gives a red coloration with ferric chloride, and is precipitated by acetate of lead.

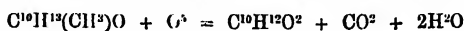
The constitution of thymohydroxycumic acid has not been definitely established, but it may be represented either by the formula $\text{C}^6\text{H}^7(\text{CO}^2\text{H})(\text{OH})(\text{C}^4\text{H}^7)$, or by $\text{C}^6\text{H}^7(\text{CH}^3)(\text{OH})(\text{C}^4\text{H}^5\text{O}^2)$.

Dibromthymohydroxycumic acid, $\text{C}^{10}\text{H}^{10}\text{Br}_2\text{O}^3$, the chief product of the action of bromine on thymohydroxycumic acid, melts under water, dissolves but sparingly therein; is very soluble in alcohol, even when dilute, and separates therefrom as an oil which solidifies in the crystalline form only after the solvent has been completely expelled by evaporation. The further action of bromine gives rise to bromophenol.

THYMOL, $C^{10}H^{14}O = C^6H^3(OH)(C^2H^7)(CH^5)$. See **PHENOLS** (p. 1544).

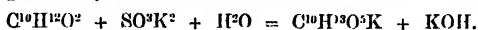
On the Violet Dye produced by the action of Nitrous Acid on Thymol, see **DYE-STUFFS** (p. 698).

THYMOQUINONE, $C^{10}H^{12}O^2$ (vii. 1156). This compound is formed by oxidising methyl-thymol dissolved in acetic acid with chromic acid mixture:

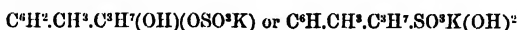


(Paternò, *Ber.* viii. 140). It may be advantageously prepared by distilling amidothymol (from nitrosothymol) with ferric chloride, the yield exceeding 50 per cent. (Armstrong, *Ber.* x. 297).

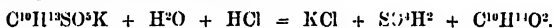
Thymoquinone is acted upon by normal potassium sulphite at 60°, the liquid on cooling solidifying to a mass of splendid crystals, which must be separated from the now strongly alkaline liquid, washed with a small quantity of ice-cold water, and quickly dried by pressure. The air-dried salt has the composition $C^{10}H^{13}O^3K$, and is formed according to the equation:



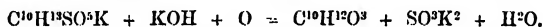
Its rational formula is either



(potassium hydrothymoquinonesulphonate), the latter being the more probable of the two. Ferric chloride colours the aqueous solution first emerald-green, then golden-yellow. Lead acetate forms with it a white flocculent precipitate insoluble in acetic acid, soluble in nitric acid; silver nitrate, a white precipitate, which soon turns black, and forms a silver speculum when heated. The salt boiled with hydrochloric acid yields sulphuric acid and thymoquinol:



Caustic alkalis induce the absorption of oxygen from the air, whereby hydroxythymoquinone is produced:



Polythymoquinone. Thymoquinone, when exposed to light, especially in thin layers, is converted into a polymeric modification, which dissolves but sparingly in all solvents, especially in ether. From alcohol it crystallises in long light yellow inodorous silky needles, which greatly resemble anthraquinone, and melt at 200°–201°. Strong sulphuric acid dissolves it without alteration at ordinary temperatures, but acts upon it at higher temperatures in the same manner as on thymoquinone. Bromine dissolved in water or in acetic acid attacks it but slightly even when heated; water, aqueous sulphurous acid, and acetic anhydride do not act upon it even at 180°. Fuming nitric acid dissolves it, but does not decompose it even at the boiling heat. By boiling it with hydriodic acid (sp. gr. 1.7) and red phosphorus, it is converted into thymoquinone; also by addition of hydrochloric acid and zinc-dust to its boiling alcoholic solution (Armstrong, *Ber.* x. 297).

Hydroxythymoquinone, $C^{10}H^{11}(OH)O^2$, is formed, as above mentioned, by the action of atmospheric oxygen on an alkaline solution of thymoquinone; also, together with dihydroxythymoquinone, by reduction of ethyl-dinitrothymol with tin and hydrochloric acid. To separate it, the tin is precipitated by hydrogen sulphide, the filtrate evaporated, and the residue crystallised from strong hydrochloric acid. The crystals, freed as far as possible from hydrochloric acid, yield by distillation with a dilute aqueous solution of ferric chloride in a current of steam, a product of oxidation which collects in the receiver, and is found to consist of hydroxythymoquinone, melting at 169°–172° (Ladenburg & Engelbrecht, *Ber.* x. 1218).

Carstanjen, who first obtained hydroxythymoquinone by the process above mentioned, and found its melting point to be 187°, is of opinion that the differences of melting point observed by himself and by Ladenburg may be due to the formation of two isomeric compounds in the above reaction. These compounds may indeed be separated to a certain extent by sublimation, the product thereby obtained consisting partly of light orange-coloured needles melting at 169°–175° (or even at 165°–166°), partly of red needles which do not melt below 183° or even 221° (*J. pr. Chem.* [2], xv. 398). Ladenburg, on the other hand (*Ber.* x. 49), ascribes the observed differences of melting point to contamination of the monohydroxythymoquinone with the dihydroxy-compound, or perhaps to the existence of a polymeric modification analogous to that of thymoquinone itself (*supra*).

Chlorohydroxythymoquinone, $C^{10}H^{10}(OH)ClO^2$, is prepared by acting on

dinitrothymol with phosphorus pentachloride, reducing the product with tin and hydrochloric acid, and oxidising the resulting amido-compound with chromic acid. 20 to 25 g. dinitrothymol are mixed in a beaker with twice the quantity of phosphorus pentachloride, and the mixture is gradually heated to 115° – 120° till the reaction begins; the heating is then discontinued as long as the reaction goes on briskly without it; and the process is terminated by renewed heating, finally to the boiling point. The phosphorus oxychloride thereby produced is distilled off in an oil-bath; the residue is poured into water; and the precipitated viscid mass, after being washed with sodium carbonate and with water, is several times crystallised from alcohol with addition of animal charcoal. The dinitrochlorocymene, $C^{10}H^{11}(NO_2)_2Cl$, thus obtained (light yellow prisms melting at 100° – 101°), is reduced by tin and hydrochloric acid, in small quantities at a time, and at the lowest possible temperature; and the resulting hydrochloride of diamidochlorocymene, after being freed from tin, and evaporated to dryness, is oxidised with a mixture of 2 pts. potassium dichromate and 3 pts. strong sulphuric acid,—about 3 g. of the amido-compound dissolved in a large quantity of water being distilled with the oxidising mixture, likewise diluted with a large quantity of water. The substance which then separates from the water in the receiver may be separated by fractional crystallisation into hydroxythymoquinone and an easily soluble chlorinated body, which latter may be purified by long-continued sublimation on the water-bath in watch-glasses covered with inverted beakers. The first sublimate thus obtained are nearly free from chlorine; and on continuing the sublimation till the sublimate and residue are found to melt at the same temperature (120° – 122°), and crystallising the residue from alcohol, chlorohydroxythymoquinone is obtained, nearly pure, in lemon-yellow prisms, easily soluble in alcohol and ether, melting at 122° , and easily sublimable (Ladenburg a. Engelbrecht, *Ber.* x. 1218).

Dihydroxythymoquinone, $C^{10}H^{10}(OH)_2O^2$, is produced by boiling a solution of chlorhydroxythymoquinone in potash, and is obtained by treating the solution with excess of hydrochloric acid, and repeatedly crystallising the resulting precipitate from alcohol, in cherry-red prisms. It melts at 220° , sublimes undecomposed, is sparingly soluble in alcohol, very sparingly in water. Ammonia and potash dissolve it with violet colour. The dilute ammoniacal solution is not precipitated by barium chloride, nor the potash-solution by alum (Ladenburg a. Engelbrecht, *loc. cit.*)

The same dihydroxythymoquinone is formed as a bye-product in the preparation of monohydroxythymoquinone (*supra*), and is also formed by treating the mono-derivative successively with ethyl iodide and potash; or better by boiling a concentrated solution of the mono-derivative with potash till the original violet colour of the solution is completely changed to brown-red, then precipitating with hydrochloric acid, and crystallising the precipitate from alcohol (Ladenburg a. Engelbrecht),

TIGLIC ACID, $C^8H^8O^2$. The supposition of Genther a. Fröhlich (vii. 395) that this acid—one of the products of the saponification of croton oil—is identical with methyl-crotonic acid, $CH^3.CH=CH.CO.OH$, has been confirmed by the experiments of E. Schmidt (*Ber.* x. 835). The two acids agree in crystalline form and optical properties, melt at 64° , and boil between 196° and 197° ; their barium and calcium salts also agree in character. Both acids fused with potassium hydroxide yield propionic and acetic acids. Bromine converts them both into dibromovaleric acid; with hydriodic acid they yield iodovaleric acid. According to Schmidt a. Berendes (*Liebig's Annalen*, xcvi. 94), *barium tiglate* forms nodular groups of small laminar crystals, but sometimes crystallises in more compact form; it has the composition $(C^8H^7O^2)^2Ba.4H^2O$, and effloresces easily. The *calcium salt*, $(C^8H^7O^2)^2Ca.3H^2O$, forms laminæ or stellate groups of small white opaque needles, and is less soluble in water than the barium salt.

In the portions of croton-oil boiling at higher temperatures than tiglic acid, Schmidt found a liquid having the composition $C^8H^{10}O^2$. The portion of the oil boiling between 174° – 175° gave with lime a crystallised salt, consisting of a compound of valerate and tiglate of calcium.

Tiglic acid is also produced, together with angelic acid, by saponification of Roman chamomile oil, and, as observed by Demarçay (p. 86), by the action of heat or of strong sulphuric acid on angelic acid. The acid obtained from Roman chamomile oil melts at 64.5° , and boils at 198.5° . Its *calcium salt*, $(C^8H^7O^2)^2Ca.3H^2O$, crystallises in white laminæ, which dissolve sparingly in cold and freely in boiling water. The *barium salt*, $(C^8H^7O^2)^2Ba.4H^2O$, is more soluble than the calcium salt, but much less soluble than the corresponding salt of angelic acid. It forms small hard prismatic crystals. The *silver salt* is less soluble than that of angelic acid, but may be crystallised from boiling water in small white feathery groups. The *potassium salt* crystallises readily in tufts of small needles which are not deliquescent (H. Kopp, *Liebig's Annalen*, xcvi. 81).

TIMBO. The root bark of the Timbo tree (*Paullinia pennata*, Linn.) contains starch, a resin, a volatile oil, tannin, an organic acid, traces of grape-sugar, and an alkaloid called *timbonine*, the sulphate of which crystallises in white needles (Martin, *Pharm. J. Trans.* [3], vii, 1020).

TIN. *Occurrence.*—Lockyer has observed in the solar spectrum a line indicating the presence of tin in the sun (*Proc. Roy. Soc.* xxvii, 279). Metallic tin in small laminae has been found by Frenzel (*Jahrb. f. Min.* 1873, 802) in bismuth-spar from Mexico.

In the form of stannic oxide, SnO_2 , tin occurs in various lithia-micas, as in the lepidolite of Paris in the State of Maine, and of Rozena in Moravia, the silica of these minerals being partly replaced by the stannic oxide (Sandberger, *Jahrb. f. Min.* 1878, 291, 657).

Stannic oxide (tinstone) occurs in the kaolins of the Department Allier in France. The levigated sand contains 18.3 per cent. SnO_2 , together with a small quantity of titaniferous iron; the unlevigated sand 0.05 per cent. Moreover, the rocks from which the kaolin has been formed contain tin; thus a quartz-like rock occurring in veins was found to contain 0.02 per cent., and a hornblende rock 0.04 per cent. tin (De Gouvenain, *Compt. rend.* lxxviii, 1032).

Two samples of tinstone from the mines of Lampiglia in Tuscany, which were worked by the ancient Etruscans, and have lately been reopened, have been analysed by C. Blanchard (*Dingl. pol. J.* cxxiv, 653) with the following results:

SnO_2	Fe_2O_3	CaCO_3
92.40	3.49	$3.34 = 99.23$
75.18	4.00	$19.64 = 98.82$

A rich deposit of tin-ore occurs at Mount Bischoff in Tasmania (Ulrich, *Jahrb. f. Min.* 1877, 494). The occurrence of tin-ore in Australia is described by Gregory and Ulrich (*Geol. Soc. Qu. J.* xxix, 1, 5; *Sill. Am. J.* [3], v, 137).

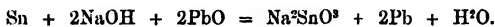
Extraction.—A report by Th. Goldschmidt, on the extraction of tin from its ores, is given in Hofmann's *Entwicklung der Chemischen Industrie*, p. 986.

Methods of obtaining tin in the pure state appear to have been known to the ancient Egyptians, as a white metal found in the wrappings of an Egyptian mummy of the age of at least 600 or 700 years B.C. was found to consist of pure tin (Church, *Chem. News*, xxxvi, 168).

Banca tin contains only very small quantities of foreign substances. Vlandereen (*Dingl. pol. J.* cxxix, 276) found in samples obtained from various districts, at most 0.175 per cent. iron, and 0.0099 sulphur, no arsenic, and mere traces of carbon; traces of lead were found only in the tin from the district of Djeboc.

Recovery of Tin from Tin-plate cuttings.—Moulin and Dolé (*Ber.* vi, 1138) extract the tin from these cuttings by passing gaseous hydrogen chloride into chambers loosely filled with them. As soon as the iron begins to be attacked, the stream of gas is interrupted, the tin chloride produced is dissolved out by water, and the tin is precipitated from the solution by zinc or iron. The precipitated powder, after being washed with dilute sulphuric acid and water, is dried and melted.

Two other methods of effecting the extraction are described by E. Kopp (*Amer. Chemist*, v, 292). (1). The cuttings are boiled in soda-ley, and litharge is added by successive portions, whereby the tin is dissolved, and lead is precipitated, according to the equation:



If care be taken that the solution finally retains a small quantity of lead oxide, the whole of the tin may be separated from the iron. The residual mixture of iron and spongy lead is levigated, and the lead thereby separated is re-oxidised in iron pans. The plumbiferous solution of sodium stannate is finally made to act on a fresh portion of tin-plate cuttings, whereby it is completely freed from lead. It is then evaporated down, and the sodium stannate thus obtained is sold for use in dye-works. (2). The tin is subjected to the action of chlorine gas, whereby it is volatilised as stannic chloride even at ordinary temperatures, while the iron remains unaltered.

S. Keith effects the separation of the tin by immersing the cuttings in an alkaline liquid, and making them serve as the positive electrode of a dynamo-electric circuit (*Deutsche Industrie-Zeitung*, 1877, 455).

On the Purification of melted Tin by Filtration, see Carter (*Dingl. pol. J.* cxxv, 469; *Jahresh. f. Chem.* 1876, 1016).

A method of obtaining Crystals of Tin by Electrolytic action is described by F. Stolba (*Ber. d. Königl.-höhm. Gesellsch. d. Wissensch.* 7 Nov. 1873; *Jahresh. f. Chem.* 1873, 282).

Grey and Brittle Modification of Tin.—The conversion of ordinary tin into this modification, noticed by Fritzsche and Oudemans (vii. 1157), has also been observed in the pyrotechnic laboratory at Spandau, where considerable quantities of tin in sheet and blocks became brittle and more easy to pulverise and more soluble in hydrochloric acid than ordinary tin. This tin contained only traces of foreign metals, and was quite free from stannic oxide, and from sulphur and phosphorus (*Ann. Phys. Chem.* [2], ii. 304; *Phil. Mag.* [5], iv. 158). The same alteration has been observed by A. Schertel (*J. pr. Chem.* xix. 322) in a tin medal and some rings, which had been kept for some centuries in a wooden box in the cathedral of Freiberg. The altered metal, which consists of nearly pure tin free from lead and containing only traces of iron and sulphur, has a reddish-grey colour, and is so brittle that it may be crushed between the finger-nails; but on drenching the pieces with hot water, they immediately acquire a lighter colour and much stronger cohesion; strong pressure or a heavy blow likewise brings out immediately a whiter colour. The specific gravity of the altered metal was only 5.8, but increased to 7.3 when the lumps were immersed in hot water. A specimen of disintegrated Banca tin, received from Fritzsche, exhibited nearly the same behaviour; its sp. gr. was 6.0, and increased on immersion in boiling water to 7.25. A further peculiarity in this latter specimen was the greater facility with which it passed from the grey into the white modification, heating for an hour and a half in ether-vapour, being sufficient to effect the conversion, whereas the Freiberg tin under these circumstances remained unaltered even after three hours, and did not acquire the density of 7.3 till it had been heated to 5.9° (in vapour of acetone). The grey modification is electro-negative to the white in dilute potash-solution, positive in dilute nitric acid.

Estimation and Separation.—Pellet a. Allart (*Bull. Soc. Chim.* xxvii. 438) estimate tin volumetrically by means of standard solutions of ferric or cupric chloride.

For the assay of tin ores, A. E. Arnold (*Chem. News*, xxxvi. 238) reduces the stannic oxide with hydrogen at a moderate red heat, and determines the loss of weight. The metallic tin is dissolved in ferric chloride, and the amount of ferrous oxide thereby formed is determined by titration.

Separation from Arsenic and Antimony.—Tin is completely precipitated from solution in aqua regia by sulphuric acid, phosphoric acid, ammonia, alkaline carbonates, and potassium cyanide, whereas solutions of antimonic acid, if prepared with tartaric acid, give no precipitate with either of these reagents. For quantitative separation, however, the only suitable reagent is *potassium cyanide*, as it is the only one which precipitates the tin completely as stannic oxide without at the same time throwing down part of the antimony. The precipitated stannic oxide is difficult to filter, but the filtration may be facilitated by addition of calcium chloride, in such quantity that the calcium carbonate subsequently precipitated by potassium carbonate may amount to about fifteen times the quantity of the stannic oxide. The following mode of conducting the process is given by Cl. Winckler (*Zeitschr. anal. Chem.* 1875, 156): The compound to be analysed, if an alloy, is dissolved in aqua regia, with addition of tartaric acid, or if it contains the metals in the form of sulphide, it is dissolved in dilute potash-ley; bromine is added in slight excess; the solution is neutralised with hydrochloric acid, and diluted to 300–400 c.c.; the necessary quantity of calcium carbonate is then added; and the solution is neutralised with potassium carbonate, mixed with potassium cyanide, and finally with a slight excess of potassium carbonate in order to complete the precipitation of calcium, after which the liquid is heated to boiling, and passed through a filter without previous stirring up of the precipitate. This last operation is once repeated with fresh water, and the precipitate which remains in the beaker is dissolved in a small quantity of strong hydrochloric acid, and again precipitated with cyanide and carbonate of potassium. By this treatment, the whole of the antimony and arsenic are obtained in the filtrate, while the precipitate—after being well washed and dried (the filter being burnt), and very strongly ignited in a porcelain crucible—contains the stannic oxide in the insoluble form, together with calcium carbonate, which may be easily separated from the stannic oxide by treatment with dilute nitric acid.

From arsenic alone tin may be separated by precipitating the two metals with hydrogen sulphide, and boiling the precipitate with water, whereby the sulphides are converted into oxides, of which that of arsenic is soluble, while the tin oxide is insoluble. Care must be taken that the mixed sulphides, immediately after precipitation, are completely freed from adhering acid by washing with water. They are then to be boiled in a flask with a large quantity of water as long as hydrogen sulphide continues to escape; or the operation may be accelerated by using a retort, through which a stream of air is passed. The same method may be applied to the quantitative separation of arsenic from all the other metals which are precipitated by hydrogen sulphide (De Clermont a. Frommel, *Compt. rend.* lxxxvi. 828).

Alloys. The arsenide of tin, Sn^3S^3 , formed by fusing the two metals together under boric oxide, is brittle, crystalline, and has a density of 6.56 (Descamps, *Compt. rend.* lxxxvi. 1065).

On the physical properties and composition of alloys of Tin and Copper, see pp. 563-566.

Tin and Lead.—The action of distilled water, vinegar, and solution of common salt on these alloys has been examined by F. Knapp (*Dingl. pol. J.* cxxx. 446), who finds, in accordance with former investigators, that the alloy composed of 4 pts. tin and 9 lead withstands the action of these liquids better than alloys containing larger proportions of tin. In general, the quantities of metal dissolved out from these alloys, even under unfavourable conditions of experiment, were quite insignificant, so that there is really nothing to fear from the use of culinary vessels made of them. On the action of Water and Saline Solutions on these Alloys, see also Bessnou (p. 1167). R. Weber (*Dingl. pol. J.* ccxxii. 153, 264; *Chem. Soc. J.* 36, 390) finds that when alloys of lead and tin, or of lead, tin, and antimony, are treated with vinegar, the quantities of metal dissolved decrease rapidly as the proportion of tin in the alloy increases. In treating the alloys with vinegar a second time, the total quantity of metal dissolved is less, but it contains a larger proportion of tin, because a portion of the lead dissolved in the first instance is precipitated by the action of the alloy on the metalliferous vinegar.

Stannic Bromide, SnBr^4 (v. 806). Carnelleya, O'Shea (*Chem. News*, xxxvi. 264) prepare this compound by acting on tin in a W-shaped tube with bromine. When purified by distillation, it forms a colourless liquid which solidifies to a mass of colourless crystals. It melts at 30° , boils without decomposition at 201° , does not fume, but slowly decomposes in contact with the air; dissolves in water without immediate decomposition. Its vapour-density, determined by Dumas' method, agrees with the molecular formula SnBr^4 (*Chem. Soc. J.* xxxiii. 55).

The double salt, $\text{SnBr}^4 \cdot 2\text{NH}^4\text{Br}$, crystallises in combinations of the cube and octahedron. Sp. gr. = 3.505 (Topsoë, *Wien. Akad. Ber.* [2 Abth.], lxi. 261).

Chlorides. The vapour-density of stannous chloride was found by Rieth (*Ber.* iii. 668) in two determinations to be 7.47 and 6.88 [$\text{H} = 1$], agreeing nearly with the molecular formula SnCl^2 , which requires 6.53. V. and C. Meyer, on the other hand (*Ber.* xii. 1195), find it to be 12.85 at 619°C . and 13.08 at 697° , leading to the formula Sn^2Cl^4 , which requires 13.06. They are of opinion that the lower numbers obtained by Rieth were due to the circumstance that he employed too high a temperature, at which the stannous chloride underwent dissociation; they find, indeed, that it gives off chlorine at a bright red heat. Carnelley, on the other hand (*Chem. Soc. J.* xxxvi. 1014), considers that the results obtained by V. and C. Meyer are not quite conclusive as to the vapour-density of the compound, inasmuch as they were made at temperatures too near its boiling point, 617° – 628° .

Double Salts of Stannic Chloride.— $2\text{NaCl} \cdot \text{SnCl}^4 \cdot 6\text{H}^2\text{O}$ is obtained by adding the calculated quantity of sodium chloride to an aqueous solution of stannic chloride, and separates in ill-defined crystals with dull striated faces. A salt, represented by the formula $2[\text{Na}^{0.13}(\text{NH}^4)^{0.87}\text{Cl}], \text{SnCl}^4$, was obtained by adding sodium chloride to a solution of tin in aqua regia, the ammonia being formed by the action of the nitric acid on the tin. $\text{CaCl}^2 \cdot \text{SnCl}^4 \cdot 8\text{H}^2\text{O}$ forms large, transparent, extremely deliquescent rhombohedrons. $\text{SnCl}^2 \cdot \text{SnCl}^4 \cdot 8\text{H}^2\text{O}$, striated needles or channelled prisms without definitely bounded faces (Topsoë, *Wien. Akad. Ber.* [2 Abth.], lxi. 261).

The following salts, prepared by Cleve (*Bull. Soc. Chim.* [2], xxxi. 197), are exactly analogous in constitution to the corresponding platinochlorides. The *lanthanum salt* has the composition $2\text{La}^2\text{Cl}^6 \cdot 5\text{SnCl}^4 \cdot 45\text{H}^2\text{O}$; the *cerium salt* is $\text{Ce}^2\text{Cl}^6 \cdot 2\text{SnCl}^4 \cdot 18\text{H}^2\text{O}$. The *didymium salt*, $\text{Dy}^2\text{Cl}^6 \cdot 2\text{SnCl}^4 \cdot 21\text{H}^2\text{O}$, forms large red crystals; the *yttrium salt* contains $\text{Y}^2\text{Cl}^6 \cdot 2\text{SnCl}^4 \cdot 16\text{H}^2\text{O}$.

Oxides. *Stannous oxide*, SnO , is obtained in the form of a violet-black crystalline powder, when the precipitate formed by adding potassium cyanide to a solution of a stannous salt is boiled for several days with solution of potassium cyanide (L. Varonne, *Compt. rend.* lxxxix. 360).

Stannic Oxide, SnO^2 .—The crystalline form of native stannic oxide (tin stone) has been examined by F. Becke (*Jahrb. f. Min.* 1878, 76), who finds that the ratio of the principal to the secondary axes is 1 : 0.67232. Microscopic examination of a specimen of wood-tin enclosed in quartz showed that the needle-shaped crystals, which were arranged in groups, agrees in form with needle-tin ore. A tin-stone from Schlackenwald gave by analysis 98.74 per cent. SnO^2 , 0.19 SiO^2 , 0.12 FeO , and 0.41 CaO (= 99.46). According to A. E. Arnold (*Chem. News*, xl. 25), both the native oxide and the strongly ignited artificial oxide are soluble in strong hydrochloric acid.

Chlorostannic Acid.—J. W. Mallet (*Chem. Soc. J.* **xxxv**, 524) observed in a moderately concentrated solution of stannous chloride which had been kept for a year or two in a bottle not very well closed, a layer of a translucent yellow gelatinous substance, which, when purified by washing with water and dried, had the composition $\text{SnO} \cdot \text{HCl}$, and probably the constitution of chlorostannic acid, $\text{O}=\text{Sn}(\text{OH})\text{Cl}$. When heated, and even when left in a vacuum, it splits up into SnO_2 and HCl . Its acid character is shown by its behaviour to soda and ammonia. By the former it is resolved into sodium chloride and stannic hydrate, which slowly dissolves in the excess of alkali; with ammonia, on the other hand, it forms a salt having the composition $\text{SnO}(\text{ONH})\text{Cl}$.

Organic Compounds of Tin.

On *Ferrocyanides of Tin*, see **CYANIDES** (p. 613); *Mercaptides* (p. 1276).

The crystalline forms of the stannomethyl compounds and their homologues are described by Hiortvaahl (*Compt. rend.* **lxxxviii**, 584; *Chem. Soc. J.* **xxxvi**, 518).

Stannopropyl-compounds. Some of these compounds, prepared by Cahours, have been already described (vii, 1085). The following have been obtained by Cahours a. Demarçay (*Compt. rend.* **lxxxviii**, 1112).

Stannodipropyl Diiodide, or **Stannic Diiododipropide**, $\text{Sn}(\text{C}^3\text{H}^7)_2\text{I}_2$, is obtained by the action of pure tin on propyl iodide, whereas that of an alloy of tin with 10 per cent. sodium gives rise to stannotripropyl iodide, $\text{Sn}(\text{C}^3\text{H}^7)_3\text{I}$. The diiodide, separated from the other products of the reaction by distillation in a vacuum, is a colourless strongly refractive liquid boiling at $270^\circ\text{--}273^\circ$. Alkalis convert it into the corresponding oxide, which is a white amorphous substance insoluble in water, alcohol, and ether, and this, when treated with hydrochloric acid, yields the dichloride, $\text{Sn}(\text{C}^3\text{H}^7)_2\text{Cl}_2$, which melts at $80^\circ\text{--}81^\circ$.

Stannotripropyl Iodide, or **Stannic Iodotripropide**, $\text{Sn}(\text{C}^3\text{H}^7)_3\text{I}$, formed, as above mentioned, by the action of sodium stannide on propyl iodide, may be dissolved out of the product by ether, and is obtained on distilling the residue left after the evaporation of the ether, as a colourless mobile liquid having a very pungent odour and boiling at $260^\circ\text{--}262^\circ$. It is decomposed by silver salts, yielding corresponding salts of stannotripropyl, and is converted by distillation with potash into a crystalline hydroxide, $\text{Sn}(\text{C}^3\text{H}^7)_3\text{OH}$, which unites with acids forming crystalline salts.

Isopropyl iodide, similarly treated, yields a series of tin-compounds analogous to those just described. Like other isopropyl-compounds, they are more fusible and volatile than the corresponding compounds of normal propyl. The *di-iodide* boils at $265^\circ\text{--}268^\circ$; the *dichloride* at $56.5^\circ\text{--}57.5^\circ$. **Stannic iodotriisopropide**, $\text{Sn}[\text{CH}(\text{CH}^3)_2]_3\text{I}$, boils at $256^\circ\text{--}268^\circ$.

Stannobutyl and Stannamyl Iodides (Cahours a. Demarçay, *Compt. rend.* **lxxxix**, 68). **Stannic di-iodo-diisobutide**, $\text{Sn}(\text{C}^4\text{H}_9)_2\text{I}_2$, is a colourless liquid, boiling at $290^\circ\text{--}295^\circ$, obtained by heating tin foil and isobutyl iodide at $120^\circ\text{--}125^\circ$ in a sealed tube for several hours. Ammonia and potash give a white amorphous precipitate of the hydroxide, which yields crystalline compounds with acids. The corresponding chlorine compound, $\text{Sn}(\text{C}^4\text{H}_9)_2\text{Cl}_2$, prepared by the action of hydrochloric acid on the iodo-derivative, is a colourless, mobile, heavy liquid, boiling at $260^\circ\text{--}262^\circ$ and solidifying at $5^\circ\text{--}6^\circ$ to a mass of silky needles resembling asbestos. **Stannic iodotributide**, $\text{Sn}(\text{C}^4\text{H}_9)_3\text{I}$, a colourless liquid, having an irritating odour, is obtained by heating a finely powdered alloy of tin and sodium containing 8 to 10 per cent. of the latter, metal with an excess of isobutyl iodide, and exhausting the solidified mass with ether. It boils at $284^\circ\text{--}286^\circ$, and when heated with potash gives the corresponding hydroxide, which boils at $311^\circ\text{--}314^\circ$, and forms crystalline compounds with formic and acetic acids.

The action of isopentyl or amyl iodide on tin appears to yield a mixture of *stannic di-iodo-diisopentide* and *stannic iodo-triisopentide*, which decomposes on distillation, and when treated with ammonia gives a white flocculent precipitate of the two hydroxides, which may be separated by means of ether, and yield crystalline compounds with acids. When an alloy of sodium and tin is employed, the main product of the reaction is *stannic iodo-triisopentide*, $\text{Sn}(\text{C}^5\text{H}_{11})_3\text{I}$, an almost colourless liquid, having a feebly irritating odour and boiling at $302^\circ\text{--}305^\circ$. The action of potash yields the hydroxide $\text{Sn}(\text{C}^5\text{H}_{11})_3\text{OH}$, a colourless, limpid, heavy liquid, which boils at $335^\circ\text{--}338^\circ$ with partial decomposition, and forms crystalline compounds with formic and acetic acids.

From the stannic methides to the stannic pentides, the stability of the compounds gradually decreases and their odour becomes less irritating.

Stannophenyl Compounds (Aronheim, *Ber.* x. 2228; xi. 2285; *Liebig's Annalen*, xciv. 145). These compounds are prepared by the mutual action of mercury-diphenyl and stannic chloride in boiling ligroin, the liquid after twelve hours being filtered and distilled in a paraffin-bath at a temperature not exceeding 150° – 160° . On pouring the residue into water which is kept cool, the ligroin separates out, while stannic chloride, hydrochloric acid, and stannic diphenylchloride remain in solution. On heating this solution, the stannic diphenylchloride or dichlorophenide, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$, is precipitated as an oily liquid, and the liquid decanted from it deposits, on further warming, sticky pulverulent substances which, after being heated for two hours, may be collected on separate filters. The first portion (m. p. 175°) consists of stannic diphenylchloride and the corresponding hydroxychloride; the second (175° – 187°) of the nearly pure hydroxychloride; the third of an infusible mixture of oxychloride, stannic diphenyloxide and stannic oxide. By washing with alcohol and prolonged suspension in water, the second portion is converted into perfectly pure stannic diphenylhydroxychloride, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClOH}$, melting at 187° .

Stannic Diphenylchloride, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Cl}_2$, crystallises in colourless triclinic prisms, in which, according to Arzruni's measurements, $a = 62^{\circ} 47'$; $\beta = 76^{\circ} 48'$; $\gamma = 94^{\circ} 3'$; $a : b : c = 0.5877 : 1 : 1.0666$. Observed forms: ∞P_{∞} , $\infty \bar{P}_{\infty}$, $0P$, P_{∞} , $\infty P'$, $\infty \bar{P}'$, 4. Measured angles: $\infty P_{\infty} : \infty \bar{P}_{\infty} = 87^{\circ} 45'$; $\infty P_{\infty} : P_{\infty} = 77^{\circ} 14'$; $\infty \bar{P}_{\infty} : 0P = 62^{\circ} 55'$; $P_{\infty} : \infty \bar{P}_{\infty} = 53^{\circ} 40'$. The chloride distils with partial decomposition at 333° – 337° , the oily distillate remaining liquid for several weeks. It dissolves easily in ether, alcohol, and ligroin, less easily and with partial decomposition in water. It crystallises best from ligroin; the prisms effloresce very easily on some of their faces. By moisture the chloride is converted into the hydroxychloride; by alkalis into the oxide; by hydriodic and hydrobromic acids into the chloriodide and chlorobromide respectively. Sodium-amalgam converts the chloride dissolved in ether into stannic triphenylchloride, $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$, melting at 106° . Concentrated acids split up the chloride into benzene and inorganic tin-salts or stannic acid.

Stannic Diphenylhydroxychloride, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClOH}$, is an amorphous powder which does not dissolve in the ordinary solvents. Strong hydrochloric, hydrobromic, and hydriodic acid convert it into the corresponding halogen-compounds; strong nitric and sulphuric acid decompose it; hydrogen sulphide does not act upon it. **Stannic diphenyliodide** is very unstable, and is immediately converted by the excess of hydriodic acid into stannic iodide and benzene: $\text{Sn}(\text{C}_6\text{H}_5)_2\text{I}_2 + 2\text{HI} = \text{SnI}_4 + 2\text{C}_6\text{H}_6$. The **chlorobromide**, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClBr}$, after standing for some time, suddenly solidifies to a crystalline mass of stony hardness, consisting of pinacoids with apparently rhombic end-faces; it resembles the chloride, and melts at 39° ; its odour, like that of the chloride, is pungently sweetish; in contact with water it crumbles to a white powder.

Stannic Diphenylchloriodide, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClI}$, is very easily decomposed by water, but very stable in the dry state. From its brownish solution in ether it separates in yellow monoclinic crystals, which become perfectly white on exposure to the air; they melt at 69° . This compound is most conveniently prepared by passing dry hydrogen iodide over the crystallised dichloride; the yield, however, is indifferent at the best; a thickish oil is obtained as secondary product. The **chlorobromide** may be prepared in a similar manner.

Stannic Diphenyldibromide, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{Br}_2$, is obtained by treating the oxide with hydrobromic acid at a gentle heat, first as a colourless oil which solidifies when touched with a crystal of the bromochloride; it melts at about 38° . The action of hydriodic acid on stannic diphenyloxide gives rise to benzene and stannic iodide.

Stannic Diphenyl-diethoxide, $\text{Sn}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)_2$, is obtained by the action of sodium-amalgam on the dichloride dissolved in ether-alcohol, and separates from the solution in cubic crystals which melt at 124° , and are decomposed by water, with formation of stannic diphenyloxide.

Stannic Triphenylchloride, $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}$, obtained, as already mentioned, by the action of sodium-amalgam on an ethereal solution of the dichloride, forms large white crystals which, after repeated crystallisation, melt at 100° . Its preparation succeeds only when the sodium-amalgam used contains a certain quantity of moisture. It is also produced when ammonia gas is passed over the fused dichloride. From the stone-hard product alcohol extracts the triphenylchloride and sal ammoniac. A secondary product is also formed, consisting of a sparingly soluble white tin-compound from which water extracts the **hydroxychloride**, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClOH}$; the compound in question is perhaps an amidochloride, $\text{Sn}(\text{C}_6\text{H}_5)_2\text{ClNH}_2$.

Stannic Triphenyloxide also forms salts with oxygen-acids, and when treated with potash yields the hydroxide $\text{Sn}(\text{C}^6\text{H}_5)_3\text{OH} + 1\frac{1}{2}\text{H}_2\text{O}$, which melts at 117° – 118° , and gives off 1 mol. water at 120° .

TITANIUM. At. w. = 50. This element appears to exist in small proportion in the atmosphere of the sun, its presence being indicated by certain dark bands in the ultra-violet portion of the spectrum (Cornu, *Compt. rend.* lxxxvi. 101, 983). It has been found by Schuhmacher (*Jahrb. f. Min.* 1878, 817) in a vesuvian occurring at Rammelsberg in Silesia, in which it appears to replace isomorphously an equivalent quantity of silicon (see *VESUVIAN*). On the occurrence of titanium as oxide and as ferrosuferric titanate, see pp. 1979, 1980.

Preparation.—S. Korn (*Chem. News*, xxxiii. 57) prepares metallic titanium by passing the vapour of the tetrachloride through a heated bulb-tube containing lumps of sodium, separating the resulting mixture of sodium chloride and titanium with cold water, washing the residual titanium with ether, and drying it over sulphuric acid. Thus prepared, it does not act upon water at any temperature below 500° . Wehrlin a. Giraud (*Compt. rend.* lxxxv. 288) fuse potassium-titanium fluoride with an equal weight of iron-filings, the iron then combining with the liberated titanium, which may be easily isolated by treating the product with hydrochloric acid.

Detection.—In testing an iron ore containing phosphoric acid for titanium, E. H. Bogardus (*Sill. Am. J.* [3], viii. 334) noticed the following reactions: 1. The presence of phosphoric acid appears to prevent the precipitation of titanic acid from its acid solution on boiling. 2. Titanic acid colours turmeric paper brown or orange like boric acid. 3. In presence of phosphoric acid and iron, titanic acid is precipitated from an acid solution by hydrogen sulphide.

Estimation.—W. Bettel (*Chem. News*, xxviii. 93) estimates titanium in minerals by fusing the finely pulverised substance with acid potassium sulphate in a platinum crucible at a heat slowly raised to redness, till the mass passes into the state of tranquil fusion; digest the mass, after cooling, with a moderate quantity of water; filters from separated silica; dilutes with water; adds sulphurous acid till all the iron is reduced; and boils the solution for six hours, renewing the water as it evaporates, after which the separated titanic oxide is collected on a filter, dried, ignited, and weighed.

A. Knop (*Zeitschr. Kryst.* 1, 58) points out that the ordinary methods of estimating titanium do not give exact results, and that the presence of titanium in siliceous minerals and rocks is often overlooked: he finds, however, that correct results may be obtained by the following method. The ammonia precipitate, consisting of ferric oxide, alumina, and titanic oxide, is filtered, washed, ignited, and weighed, then fused with acid potassium sulphate; the melt is dissolved; the solution mixed with tartaric acid, and made alkaline with ammonia; and the iron precipitated by ammonium sulphide. The filtrate is next evaporated to dryness; the residue ignited and mixed with strong sulphuric acid, which completely removes any blackening produced by the tartaric acid, and not previously removed by the ignition; then treated with excess of caustic soda-solution, which dissolves the alumina, leaving sodium titanate to be again fused with potassium sulphate. On dissolving the melt in water and boiling the solution, titanic oxide remains behind. By this method Knop has demonstrated the presence of considerable quantities of titanium in the melanites of the Kaiserstuhl range, and of Frascati near Rome, and in pyroxene from the former locality.

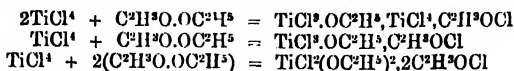
For the estimation of titanium when associated with zirconium, as in astrophyllite, arfvedsonite, and zircon, the following colorimetric method is employed by G. A. König (*Zeitschr. Kryst.* i. 423). The mixture of titanic oxide and zirconia obtained by the ordinary method of analysis having been weighed, a blowpipe-bead weighing 0.65 mg., prepared from 0.12 mg. phosphorus-salt, is coloured with 2 mg. of the mixture, and its tint is compared with those of a series of 10 or 20 test-beads likewise coloured by 2 mg. of oxide containing from 0 to 100 per cent. Al_2O_3 and 100 to 0 per cent. TiO_2 . This method admits of the estimation of 5 or even 2.5 per cent. TiO_2 in the bead.

Chlorides. The Tetrachloride, TiCl_4 , or Titanic Chloride, may be prepared by passing the vapour of carbon tetrachloride over small lumps of titanic oxide placed in a tube heated to bright redness, the titanic chloride thus obtained amounting to about 50 per cent. of the carbon tetrachloride used. The same result may be more economically obtained by using, instead of the carbon tetrachloride, a mixture of carbon monoxide and chlorine in equal volumes (C. W. Watts a. C. A. Bell, *Chem. Soc. J.* 1878, xxxiii. 443).

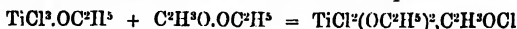
Titanic chloride is decomposed by sulphuric hydroxychloride, $\text{SO}_2(\text{OH})\text{Cl}$, with

formation of a yellow amorphous deliquescent powder having the composition $\text{ClSO}^2\text{.OTiCl}^3$ (Clausnizer, *Ber.* xi. 2011).

Compounds of Titanic Chloride with Ethers (Demarçay, *Bull. Soc. Chim.* [2], xx. 127; *Compt. rend.* lxx. 1414). Titanic chloride unites directly with the ethers of organic acids, also with *ethyl mercaptan* and *ethyl sulphide*, forming compounds which, according to Demarçay, are constituted according to the formulæ on the right-hand sides of the following equations. With *ethyl acetate* the three following compounds are formed :



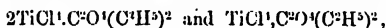
Demarçay rests his view on the observation that the compound $\text{TiCl}^3(\text{OC}^2\text{H}^3)$ unites directly with acid chlorides, and with titanice chloride, forming the compounds above mentioned : thus with ethyl acetate it forms the compound



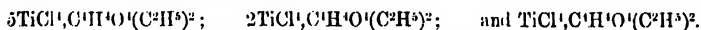
intermediate between the last two in the preceding series.

With *ethyl benzoate* three compounds are also formed, which are more stable and crystallise better than the acetyl-compounds, but are decomposed by water, with formation of benzoic acid and ethyl benzoate. The formulæ are the same as those above given, substituting $\text{C}^7\text{H}^5\text{O}$ for $\text{C}^2\text{H}^3\text{O}$. There is also a compound, $\text{TiCl}^2(\text{OC}^7\text{H}^5\text{O})^2.\text{C}^7\text{H}^5\text{OCl}$, formed by combination of $\text{TiCl}^3.\text{OC}^7\text{H}^5\text{O}$ and ethyl benzoate.

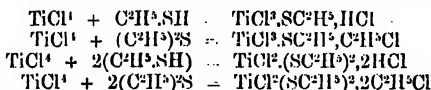
Perfectly analogous compounds are also formed with the ethylic ethers of butyric, valeric, caproic, and angelic acids, also with amyl acetate and valerate and with methyl benzoate. The ethers of bibasic acids likewise yield analogous but much less stable compounds; *ethyl oxalate*, for example, yields the two compounds



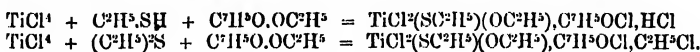
and *ethyl succinate* the three compounds



With *ethyl hydrosulphide* and *sulphide* four compounds are formed, viz. :



The first two have a blackish-red colour, and do not crystallise well; the third and fourth crystallise well, the third having a scarlet and the fourth a fine dark red colour. Lastly, the following intermediate compounds have been obtained :



The following bodies have been prepared by P. P. Bodson (*Chem. Soc. J.* 1876, xxix. 309). A compound of titanice chloride with *ethyl oxide*, $\text{TiCl}^4(\text{C}^2\text{H}^3)^2\text{O}$, is formed by mixing equal parts of the component bodies in a cooled vessel. It is a yellow crystalline body, which melts between 42° and 45° , boils at 118° – 120° , and is resolved by water into hydrogen chloride and titanice oxide. By mixing the constituents in different proportions the compound $2\text{TiCl}^4.3(\text{C}^2\text{H}^3)^2\text{O}$ is obtained. *Titanic Ethyltrichlorhydrin*, $\text{TiCl}^3(\text{OC}^2\text{H}^3)$, is obtained from the residues left in the preparation of the last-mentioned compound, by the application of a strong heat, or in larger quantity by heating the mixture of ether and titanice chloride in an oil-bath. When pure it forms a crystalline mass, melts at 56° – 78° , and boils at 186° – 188° .

The *Hydrochloride of Titanic Triethylchlorhydrin*, $\text{TiCl}^3(\text{OC}^2\text{H}^3)^3.\text{HCl}$, is obtained by the action of titanice chloride (1 mol.) on absolute alcohol (4 mol.), the mixture being heated in a water-bath at 80° – 100° , the excess of alcohol, after the action is over, being removed by distillation, and the remaining white crystalline mass recrystallised from alcohol. It forms white crystals, which melt between 105° and 110° , and are decomposed by water. On dissolving it in alcohol and adding a very dilute alcoholic solution of sodium ethylate, sodium chloride separates out, and the liquid contains ethylic titanate, $\text{Ti}(\text{OC}^2\text{H}^3)^4$, which crystallises easily in deliquescent needles, and is converted by addition of water to its ethereal solution, into titanice hydroxide, $\text{Ti}(\text{OH})^4$, which is precipitated (Demarçay, *Compt. rend.* lxxx. 51).

Trichloride, TiCl^3 , and *Dichloride* or *Titanous Chloride*, TiCl^2 (Friedel & Guérin, *Compt. rend.* lxxxi. 889).—The trichloride (also, though erroneously, called

sesquichloride) is formed by heating the tetrachloride with reduced silver in a sealed tube, but cannot be separated from the silver chloride formed at the same time, either by solvents or by distillation. On distilling the mixture, the tetrachloride passes over, and metallic silver remains behind. The trichloride is not volatile as stated by Ebelmen. When it is heated in a stream of hydrogen to the temperature of boiling sulphur, at which the tetrachloride is not attacked by hydrogen, the tetrachloride passes over, and a black substance remains, consisting of the dichloride. It is probably this latter compound which in the experiment above described effected the reduction of the silver chloride to metallic silver.

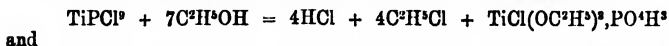
A *hydrated trichloride*, $Ti^2Cl^3 \cdot 8H^2O$, is formed when the violet solution obtained by the action of hydrochloric acid on titanium is evaporated to the crystallising point. It oxidises with extraordinary facility, with continuous separation of finely divided titanic oxide (Glatzel, *Ber.* ix. 1829).

Titanium dichloride is very difficult to obtain pure, as it is very apt to be contaminated either with a small quantity of oxychloride or of unaltered trichloride. To obtain a pure product it is indispensable to proceed as follows. The trichloride having been prepared by the action of hydrogen on the tetrachloride, the hydrogen is displaced by a stream of carbon dioxide, the trichloride is then introduced into a tabulated retort previously filled with carbon dioxide, and this gas is again displaced by hydrogen. The retort is then placed on a sand-bath, and the bath is heated to dull redness, while a continuous stream of hydrogen is passed through the retort. When the whole of the tetrachloride has been distilled over, the residue is left to cool, the hydrogen is displaced by carbon dioxide, and the residual dichloride is transferred to tubes filled with the same gas. The dichloride in cooling absorbs hydrogen, and unless this gas is expelled the compound will take fire on exposure to the air (Friedel a. Guérin).

Titanium dichloride thus prepared is a black light substance, which greedily absorbs moisture, being thereby converted into a kind of mud. When thrown into water it hisses like red-hot iron, and if touched with a drop of water takes fire. It quickly decomposes water with evolution of hydrogen, and forms a yellow liquid like that which results from the deliquescence of the trichloride in moist air. It is insoluble in ether, carbon sulphide, and chloroform. Absolute alcohol is also decomposed by it, with evolution of hydrogen, and formation of a yellowish liquid which becomes blue-black on addition of ammonia. *Bromine* combines with the dichloride, giving rise to incandescence, and forming a liquid, probably $TiCl^2Br^2$, which boils at 176° . The dichloride volatilises at a red heat in a stream of hydrogen without previous fusion. Heated in the air on platinum-foil, it burns like tinder, giving off vapours of the tetrachloride and leaving titanic oxide. The trichloride likewise absorbs bromine, forming a liquid, probably Ti^2Cl^3Br , which boils at 154° (Friedel a. Guérin).

Oxychloride, $Ti^2O^2Cl^2$. This compound, analogous to Ti^2Cl^6 , is formed as a secondary product in brown-red scales in the preparation of the dichloride by the method above described, especially if the precautions as to the exclusion of moisture are not very strictly observed; it may be obtained in larger quantity by exposing titanic oxide at a red heat to the action of a mixture of hydrogen and the tetrachloride. It forms red-brown rectangular laminae, apparently orthorhombic, which are not directly attacked by water or by very dilute nitric acid. On exposure to the air it gradually turns white, from formation of titanic oxide. The crystals are attacked by ammonia, turning first black and then white, without alteration of form; at the same time hydrogen is evolved (Friedel a. Guérin, *Compt. rend.* lxxxii. 509).

Phosphochlorides. The phosphochloride, $TiCl^4.PCl^3$, which Züttchen obtained by the action of PCl^3 on titanic oxide, and the phosphoroxychloride, $TiCl^4.POCl^3$, which Weber obtained by treating titanic oxide with phosphorus oxychloride (vi. 1097), may also be produced by the following reactions. The phosphochloride is directly formed by heating molecular proportions of titanic chloride and phosphorus pentachloride in sealed tubes at 150° ; the phosphoroxychloride in like manner by heating 2 mol. PCl^3 with 1 mol. TiO^2 . The latter is an easily crystallisable body, which melts at 110° and boils at 140° . Both these compounds exhibit a remarkable behaviour with alcohols. On throwing them by small portions into ethyl or methyl alcohol, reactions take place, represented by the following equations:



and



After removal of the alcohol, there remains a gummy mass which has a metallic taste, and is decomposed by water into hydrochloric acid, and a compound,

$\text{TiO}(\text{OC}^2\text{H}^3)_2\text{PO}^4\text{H}^3$, insoluble in water and in ether, but soluble in alcohol. On heating this compound, ethyl chloride is first given off, then ether, and there remains a compound of titanic oxide with phosphoric acid, $\text{TiO}^2_2\text{PO}^4\text{H}^3$ (Wehrlin a. Giraud, *Compt. rend.* lxxxv. 288).

Nitrides. Two of these compounds are known, viz., Ti^3N^1 and Ti^2N^2 . The first, analogous in constitution to TiCl^4 and TiO^2 , was discovered by Wöhler & Deville, who obtained it by heating potassium-titanium fluoride, or the corresponding sodium-compound, in nitrogen-gas (v. 841). It crystallises in copper-coloured crusts, which when examined by the microscope exhibit triangular summits, apparently belonging to a rhombohedron. When ignited in hydrogen, or even in ammonia-gas, it is easily converted into Ti^2N^2 .

This latter compound, $\text{N}\equiv\text{Ti}-\text{Ti}\equiv\text{N}$, analogous to Ti^2Cl^4 , is produced by strongly igniting the sesquioxide or dioxide of titanium for several hours in a current of perfectly dry ammonia-gas. The product is an amorphous brass-yellow powder, having a density of 5.28 at 18° , and hard enough to scratch topaz. When suspended in water it is transparent with a blue colour, but appears yellow by reflected light. It is converted into titanic oxide by ignition in the air, and is attacked by melting potash, with evolution of ammonia. The same compound is obtained, mixed with charcoal, when titanic oxide is heated to bright redness in cyanogen-gas. It is also frequently produced as a brass-yellow film in the preparation of titanium trichloride, when due precaution is not taken to exclude nitrogen from the apparatus (Friedel a. Guérin (*Compt. rend.* lxxxii. 972).

On *Titanium Ferrocyanides*, see p. 613.

Oxides. *Sesquioxide*, Ti^3O^3 .—This oxide is one of the secondary products obtained in the preparation of the dichloride by heating the trichloride in hydrogen gas (p. 1978) when the air is not completely excluded. A portion of the tube and the boat containing the trichloride then become coated with small, shining, copper-coloured crystals having a violet reflex, and appearing under the microscope as hexagonal laminae, exactly similar in form to iron-glance from Elba, Fe^2O^3 , and to ilmenite, FeTiO^3 . The isomorphism between ferric oxide and titanium-compounds here exhibited is likewise seen in other compounds, as Ti^2Cl^4 and Fe^2Cl^4 , and $\text{Ti}^2(\text{SO}^4)_3$ and $\text{Fe}^2(\text{SO}^4)_3$.

Salts analogous to this oxide are formed when metallic titanium is dissolved in hydrochloric or sulphuric acid; with hydrofluoric acid, on the other hand, TiF^4 is produced (v. 840), but in no case is a salt analogous to the dichloride obtained by the action of an acid on metallic titanium. The *sulphate*, $\text{Ti}^4(\text{SO}^4)_3 \cdot 8\text{H}^2\text{O}$, crystallises readily from the violet solution obtained by treating titanium with sulphuric acid and concentrated by evaporation, in laminated groups of small crystals. By oxidation with nitric acid it is converted into titanic sulphate, $\text{Ti}(\text{SO}^4)_2 \cdot 3\text{H}^2\text{O}$, which is a perfectly transparent, somewhat yellowish, resinous mass, very hygroscopic and deliquescent. With potassium sulphate it forms the double salt, $\text{Ti}(\text{SO}^4)_2 \cdot \text{K}^2\text{SO}^4 \cdot 3\text{H}^2\text{O}$, which Warren obtained (v. 616) by fusing titanic oxide with acid potassium sulphate (Glatzel, *Ber.* ix. 1829).

Dioxide or Titanic Oxide, TiO^2 .—This oxide occurs native in the forms of Anatase, Brookite, and Rutile.

The crystalline forms of anatase from the Lorcheltiny Alp in the Binnenthal are described by C. Klein (*Jahrb. f. Min.* 1875, 337). Four types are distinguishable, according to the predominance of P, $\frac{1}{2}\text{P}$, ∞P or $\frac{3}{2}\text{P}$. The second and third types are those which have been described as *Wieserin*. The mineral occurs in clefts of a micaceous gneiss, accompanied by calcite (less frequently by arragonite), brown hæmatite, adularia, rock-crystal, mica, chlorite, iron-glance, rutile, and sometimes sphene. The specific gravities of the four types are as follows:

Type	1 (P)	2 ($\frac{1}{2}\text{P}$)	3 (∞P)	4 ($\frac{3}{2}\text{P}$)
Sp. gr.	3.87	3.97	3.83	3.860

In type 2, two kinds of onclosure were observed and distinguished as magnetic iron oxide and rutile (?), to which perhaps the higher specific gravity is due. G. vom Rath (*Jahrb. f. Min.* 1876, 64) describes anatase as a coating on adularia, rutile, and iron-glance, from Monte Carradi in the Tavetsch. A development unusual in anatase is determined by the predominance of $\frac{3}{2}\text{P}$. Anatase and Brookite from the gneiss of the Pitschin Joch, Tyrol, are described by A. Brezina (*ibid.* 1873, 645).

Anatase and Brookite have been found by Klette (*Zeitschr. geol. Ges.* xxvii. 442), together with quartz and magnesia mica, in a druse of orthoclase from Wolfshau, near Schmiedeberg, in Silesia.

The crystals of Brookite are referred by A. Schrauf (*Jahrb. f. Min.* 1877, 403) to three types, viz., those from Tremadoc, North Wales, those from Ulster County,

New York, and those of English, Russian, and Swiss origin. They are all referable to a monoclinic system with the following elements:

	a	b	c	Axial angle
Type I.	0.844149	: 1	: 0.93887	90° 21'
" II.	0.846931	: 1	: 0.93795	90° 39.3
" III.	0.841419	: 1	: 0.943441	90° 6.5'

Schrauf regards brookite as isomorphous with Wolfram, a relation which is best exhibited by the formula $TiTiO_4$.

A ferruginous variety of brookite occurs in clefts of the andesite of the Arany Berg in Transylvania. A. Koch (*Jahrb. f. Min.* 1878, 652), from the crystalline form and from an analysis made with a very small quantity of material, inferred that it was a rhombic modification of titaniferous iron, and called it *pseudobrookite*; but Groth (*Zeitschr. Kryst.* iii. 306), correcting Koch's crystallographic determinations, shows that by a proper selection of the axes, the crystallographic elements of the mineral come so near to those of brookite, that it may be regarded as probably a ferruginous variety of the latter. Analysis gave:

TiO_2	$FeO^{(*)}$	$CaO^{(*)}, MgO^{(*)}$	$X^{(*)}$	Sp. gr.
52.74	42.29	4.28	0.69 = 100	4.98

(*) With a little alumina: partly as FeO . (°) Determined by difference. (°) Loss by ignition.

Rutile. G. vom Rath (*Zeitschr. f. Kryst.* i. 13; *Jahrb. f. Min.* 1877, 297) describes rutile in forms of iron-glance. The small crystals from the Lärchettini Alp in the Binnenthal exhibit the combination $P. P\infty. \infty P. \infty P\infty. \infty P2$, together with a few other octagonal prisms, so placed that their principal axes are parallel to the three diagonals of the base OR_6 of the iron-glance, and the face $\infty P\infty$ is parallel to the base itself. That this peculiar formation is not a mere coating, but a true pseudomorph of rutile after iron-glance, is shown by the interior of the groups, which consists of fine-grained rutile. In the rutile from Hot Springs, near Magnet Cove, Arkansas, outcrops occur, intergrown parallel to the faces of $P\infty$, which meet in a polar edge of 45.2° , the twin-formation eight times repeated nearly forming a closed circle. V. Hansel (*Jahrb. f. Min.* 1878, 528) describes crystals of rutile from Madriach, exhibiting the combination $P. P\infty. \infty P. \infty P\infty$. G. Seligman (*Jahrb. f. Min.* 1877, 828) describes regular intergrowths of rutile with magnetic iron ore, crystallised in tabularly distorted octohedrons, the vertical combination-edges of the rutile lying parallel to the edges of the magnetic iron ore, and the face $\infty P\infty$ of the former to the predominating face of the latter. On the crystalline forms of *Ilmenorutile* from the eastern side of Lake Ilmen, see P. v. Jeremejew (*Zeitschr. Kryst.* ii. 504; *Jahresb. f. Chem.* 1877, 1277).

Titanates. *Ferroso-ferric Titanate (Titaniferous Iron)*.—A specimen of this mineral, rich in magnesium, from the diamond-bearing sand of Du Toit's Pan, South Africa (mistaken by the miners for carbon), has been analysed by E. Cohen (*Jahrb. f. Min.* 1877, 695) with the following result:

	TiO_2	FeO^*	FeO	MgO	Insol. residue	Sp. gr.
Found	52.69	6.91	26.50	11.85	2.07 = 100.02	4.436 at 14° .
Corrected	53.79	7.05	27.06	12.10	1. = 100	

Calcic Silicotitanate (Titanite, Sphene).—The following analysis by Schmöger of a titanite from the syenite granite, which forms a vein in the eclogite of Waldheim in Saxony, is published by H. Credner (*Zeitschr. geol. Ges.* xxvii. 202):

TiO_2	SiO_2	Al_2O_3	Fe_2O_3	YO	CaO
37.45	31.37	4.79	3.13	0.88	22.38 = 100

By the presence of alumina this mineral is related to the titanite, occurring in syenite near Dresden, described by Groth (*Jahresb. f. Chem.* 1866, 943), and named *Grothite* by Dana (*Mineralogy*, 5th ed., p. 386).

Light-brown to flesh-coloured titanite (*greenovite*, v. 398) occurs near Vermatt, in crystals of the combination $P\infty. - P\infty. - 2P2. - 4P4. + \frac{1}{2}P2$, together with perowskite on pennine. Manganese, the usual colouring principle of greenovite, was detected only in traces in a bright-coloured crystal, ferrous oxide somewhat more abundantly. Sp. gr. 3.547 (C. Hintze, *Zeitschr. Kryst.* iv. 310). Titanite crystals from the limestone of Ersby in Finland are described by F. J. Wük (*ibid.* 495), some of rhombohedral habit ($\infty P. OP$), others tabular from predominance of $\infty P\infty$, the former directly imbedded in the limestone, the latter surrounded by scapolite.

TOBACCO. The following observations on the composition and culture of tobacco have been made by S. W. Johnson (*Annual Report of the Connecticut Board of Agriculture*, 1873, 384).

Tobacco leaf, as sold by the farmer, contains about 30 per cent. of water. The following table shows the ash-constituents (not including sand or CO_2) and nitrogen of dry tobacco-leaf from Connecticut and Massachusetts, also the mean ash-constituents of Kentucky tobacco :

	Silica	Chlorine	Sulphuric acid	Phosphoric acid	Lime	Magnesia	Potash	Soda	Sum of ash ingredients	Nitrogen
New England tobacco :—										
Highest percentages . . .	·30	2·55	1·69	·80	8·23	2·21	7·45	1·81	19·40	5·11
Lowest percentages . . .	·05	·08	·52	·47	3·17	·94	3·90	·08	12·32	3·20
Mean (12 samples) . . .	·14	1·55	1·09	·59	5·71	1·36	5·79	·33	16·56	4·24
Kentucky tobacco :—										
Mean (30 samples) . . .	·35	·48	·54	·64	1·53	1·20	4·82	·27	12·83	—

The percentage of nitrogen is greater than in any other cultivated crop ; part of it exists as nitrates.

The composition of tobacco is very variable ; like all green crops, its constituents are much influenced by the nature of the soluble matters in the soil. According to Schlössing and Nessler, tobacco burns best when it contains considerable quantities of potassium malate ; this condition the manufacturer is able to imitate by treating the leaves with a solution of potassium acetate or of some other organic potassium salt.

The presence of chlorides is injurious to combustion, but the evil is obviated if a more than usual proportion of potassium malate is present. Sulphates rather favour and nitrates are prejudicial to proper combustion. Tobacco dried without fermentation is yellow, the depth of colour varying according to the extent of the fermentation.

A good crop of tobacco, yielding 1,260 lbs. of dry leaf and 1,100 lbs. of dry stalk, removes from the soil in lbs. per acre :—

	Sulphuric acid	Phosphoric acid	Lime	Magnesia	Potash	Soda	Sum of ash ingredients	Nitrogen
Leaves	14	7½	73	17	71	5	206	49
Stalks	3	15	15	2	47	10	95½	33
Total	17	22½	88	19	118	15	301½	82

As the stalks are returned to the land, tobacco is not a very exhausting crop, but since the period of growth is very short (three months in the middle of summer) it requires to be abundantly manured. Farmyard manure, guano, fish manure, and gypsum, with potassium salts (avoiding the chloride) under special circumstances, are said to yield good results. As the soil is for the greater part of the year unoccupied by the crop, a serious loss of nitrogen may take place by the washing out of nitrates. To avoid this it has been recommended that rye should be sown as soon as the tobacco is off, and ploughed in as a green crop when cultivation for tobacco commences.

Five sorts of tobacco analysed by E. S. Breidenbaugh (*Amer. Chem.* iii. 306) yielded the following results :

	1	2	3	4	5
SiO ² . . .	0.13	0.13	0.08	0.12	0.13
Cl . . .	0.55	0.05	1.70	0.88	1.05
SO ² . . .	0.77	0.42	1.14	0.95	0.53
P ² O ⁵ . . .	0.30	0.34	0.40	0.34	0.42
CaO . . .	4.12	1.34	2.46	5.34	4.78
MgO . . .	0.83	0.43	0.80	0.81	1.51
K ² O . . .	2.48	3.12	4.36	2.95	3.41
Na ² O . . .	1.15	0.12	0.23	0.24	0.14
Insoluble residuo . . .	2.23	3.12	1.36	1.18	1.86
H ² O . . .	38.00	59.51	33.76	36.90	27.23
N . . .	1.28	0.39	1.17	0.98	0.74
Organic Matter . . .	48.16	31.03	52.54	49.31	58.20
	100	100	100	100	100

In several varieties of tobacco consumed in Sweden, and analysed in the laboratory of Asarun, the amount of ash was found to vary from 9 to 17 per cent., and that of the constituents soluble in warm water, from 50 to 64 per cent. (*Dingl. pol. J.* cccxxv. 615).

The ash of Havannah cigars has been analysed by A. Percy Smith (*Chem. News*, xxviii. 261, 324) with the following result:

Potassium Sulphate	7.401
" Carbonate	9.012
Sodium Sulphate	5.764
" Chloride	3.272
" Carbonate	1.039
Calcium Sulphate	4.180
" Carbonate	45.400
Ferric Oxide and Phosphoric acid	0.460
Calcium and Magnesium Phosphates	9.210
Silica	9.641
Charcoal	3.162
Aluminium, Lithium Carbonate, and loss	1.459
	100.000

According to E. R. Durrwell (*Bull. Soc. Chim.* [2], xxiv. 450), the whiteness of the ash of good tobacco is due to the presence of large quantities of potassium and sodium salts, which swell up as the tobacco burns, and tear the fibres, thereby inducing complete combustion.

Proportion of Nicotine in Tobacco.—L. Ricciardi (*Ber.* xi. 1385) has determined the amount of nicotine in 20 sorts of tobacco raised in the Romagna and in Modena under various conditions of growth and with different manures. The smallest proportion (1.62 per cent.) was found in a Havannah variety; the largest (5.99 per cent.) in a Virginian variety.

Smoke of Tobacco.—G. Krause (*Dingl. pol. J.* cccxiii. 495) has examined tobacco-smoke for the oxides of Carbon. He found in the smoke of several kinds of cigars, obtained by suction either with an aspirator or by the mouth, 9.4 to 16 vol. per cent. CO², and 8.7 to 13.8 per cent. CO. The smoke of a loosely stopped pipe contained 14.7 per cent. CO², and 5.2 per cent. CO; that of a closely stopped pipe contained 9.2 per cent. CO², and 9.2 per cent. CO. H. Schwarz (*ibid.* cccxvi. 306) found in the smoke of a Virginian cigar, 12 to 12.8 per cent. CO², and 4.0 to 4.76 CO.

On the alleged presence of nicotine in tobacco-smoke, see NICOTINE (p. 1391).

TOLALLYL SULPHIDE, C¹⁴H¹⁶S (v. 850; vi. 1099). This compound, produced by the dry distillation of benzyl monosulphide or bisulphide, was said by Mürcker and by Dorn to melt at 143°–145°, by Fleischer at 166°; Forst, however, finds that after repeated crystallisation from alcohol it melts at 172°–173°. Very small quantities of stilbene lower the melting point considerably. Tolallyl sulphide is less soluble in hot water than stilbene, but dissolves somewhat more readily in ligroin, still more in ether and in chloroform, and crystallises from these solvents in loose, white, highly lustrous laminae, resembling hydrobenzoin. It sublimes without decomposition, and boils at 350°–360° (thermometer-bulb in the vapour). It does not appear to unite with picric acid. When boiled with chromic acid mixture it blackens, and yields carbonic and benzoic acids. The compound C¹⁴H¹²S, which

Barbier obtained by heating benzyl sulphide, was probably nothing but impure toluyl sulphide (Forst, *Liebig's Annalen*, clxxviii. 370).

TOLANE, $C^{10}H^{10}$. This hydrocarbon, which Limpricht & Schwanert obtained by heating toluylene bromide with alcoholic potash (vi. 1099), is also produced by the action of alcoholic potash on hydrobenzoin chloride. As thus obtained, it forms characteristic large transparent highly lustrous crystals melting at 60° . It is produced also, in like manner, though somewhat impure, from the chloride of isohydrobenzoin.

Tolane-vapour passed through a red-hot tube yields chiefly high-boiling products and much charcoal; no phenanthrene (Gräbe, *Liebig's Annalen*, clxxiv. 198). Tolane, heated to dull redness (540° – 550°) in a closed and vacuum tube, yields a small quantity of benzene, together with highly carbonised products (Barbier, *Ann. Chim. Phys.* [5], vii. 615). Heated with hydriodic acid and red phosphorus at 170° – 180° , it yields stilbene, and on further action dibenzyl (Barbier, *Compt. rend.* lxxviii. 1772).

TOLIDINE, $C^{14}H^{10}N^2$. See TOLYL-DIAZINS.

TOLLYLENE CHLORIDE syn. with **DICHLOROXYLENE**. See XYLENE-COMPOUNDS.

TOLU BALSAM. According to Baillon (*Pharm. J. Trans.* [3], iv. 385) Tolu balsam and Peru balsam are derived from the same tree, *Toluifera balsamum*, Linn., and the differences between the two products are due merely to differences in the mode of obtaining them.

TOLUALDEHYDES. The name *Aldehydine* is given by Ladenburg (*Ber.* xi. 590, 1656) to a class of compounds formed by the union of 1 mol. of an ortho-diamine with 2 mol. aldehyde, the combination being attended with elimination of 1 mol. water. Meta- and para-diamines do not form stable compounds with aldehydes. See TOLUENES (DIAMIDO-).

TOLUENE, $C^7H^8 = C^6H^5(CH^3)$. This hydrocarbon is formed, together with benzene and some of its higher homologues, by passing the vapours of petroleum and lignite tar through a red-hot tube filled with lumps of charcoal (Letny, *Ber.* xi. 1210); also by heating petroleum with aluminium chloride, in presence of oxide of zinc, iron, or lead, and air (Friedel & Crafts, *Jahresh. f. Chem.* 1878, 1166).

Reactions. 1. With *Oxygen*.—Toluene mixed with aluminium chloride absorbs oxygen, and on decomposing the mixture with water, an oily liquid is separated, from which ether extracts a cresol boiling at 200° (Friedel & Crafts, *Compt. rend.* lxxxvi. 884).

2. With *Bromine*.—Toluene, subjected to exhaustive bromination with bromine containing iodine, yields perbromobenzene and perbromomethane (p. 1067).

3. With *Hydriodic acid*.—Berthelot found that toluene heated in a sealed tube to 270° – 280° is converted into the saturated hydrocarbon heptane, C^7H^{16} (vi. 741). According to Wreden, on the other hand (*Ber.* viii. 769), the product thus obtained is not heptane, but an unsaturated hydrocarbon, C^7H^{14} . In subsequent communications, both Berthelot (*Bull. Soc. Chim.* [2], xxvi. 146) and Wreden (*Ber.* x. 712, 2241; *Liebig's Annalen*, clxxxvii. 153) adhere to their former statements, Wreden designating his hydrocarbon, C^7H^{14} , as hexhydrotoluene, and describing it as a colourless mobile liquid having a sp. gr. of 0.772 at 0° , and 0.758 at 20° , a vapour-density of 3.36 (calc. 3.38), and boiling between 94° and 100° . It is not attacked by a mixture of nitric and sulphuric acids at ordinary temperatures, but on heating it is oxidised to carbon dioxide and water.

4. By the action of *iodine chloride*, toluene is converted into *p*-iodotoluene, an oily liquid boiling at 206° .

5. Toluene mixed with *molybdenum pentachloride*, and subjected to the action of *chlorine gas* at the heat of the water-bath, is converted in the first instance into *parachlorotoluene* (b. p. 158° – 161°), mixed with only very small quantities of the *o*- and *m*-modifications, and by continued action of the chlorine into di- and trichlorotoluenes (Aronheim & Dietrich, *Ber.* viii. 1401).

6. *Chromyl chloride*, CrO_2Cl_2 , converts toluene into benzaldehyde and benzyl chloride (Etard, *Compt. rend.* lxxxiv. 127).

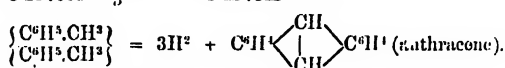
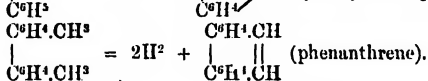
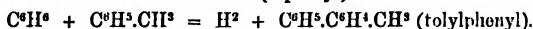
7. With *antimony trichloride* at high temperatures toluene yields nothing but tarry products.

8. By *sulphuric hydroxychloride*, $SO_2(OH)Cl$, toluene is converted mainly into *paratoluenesulphonic acid*, together with small quantities of *paratoluenesulphochloride* and *sulphotoluide*. When toluene and sulphuric hydroxychloride are mixed

together with phosphoric anhydride, the chief product obtained is paratoluenesulphochloride, together with a small quantity of sulphotoluide (Beckurts a. Otto, *Ber.* xi. 2062).

9. *Action of Heat on a Mixture of Toluene and Benzene.*—When the mixed vapours of these bodies are passed through a red-hot tube, the following hydrocarbons are formed: Benzene, naphthalene, diphenyl, paratolylphenyl, orthoparaditolyl, γ -methylene-diphenylene, δ -methylene-diphenylene, phenanthrene, anthracene, para-diphenylbenzene, a hydrocarbon having the formula $C^{12}H^{22}$, a liquid hydrocarbon boiling at 293° – 316° , and melting at 13° , two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359° – 383° and 402° – 427° respectively, and a solid black bitumene.

The more important changes occurring during this reaction may be represented as follows:

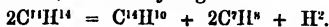


The γ - and δ -methylene-diphenylenes above mentioned are isomeric, not identical, with the methylene-diphenylenes (diphenylene-methanes),* which are obtained by passing diphenylmethane through a red-hot tube, and by reducing diphenylene ketone with zinc-dust or with hydriodic acid and red phosphorus (p. 670); also with Berthelot's coal-tar fluorene (p. 671). The distinguishing characters of the four modifications of methylene-diphenylene are exhibited in the table on p. 1985.

10. *Action of Zinc on a Mixture of Toluene and Benzyl chloride.* Benzyl-toluenes (Weber a. Zincke, *Ber.* vii. 1153). The products obtained by heating a mixture of toluene and benzyl chloride with zinc-dust consist chiefly of mono- and di-benzyl-toluene, $C^{11}H^{14}$ and $C^{12}H^{20}$, together with smaller quantities of anthracene and various volatile hydrocarbons, most probably formed by decomposition of the benzyl chloride.

Monobenzyl-toluene, or *Benzyltolyl*, $C^6H^5.CH^2.C^6H^4.CH^3$, passes over as a colourless oil boiling at 277° (vii. 283). When subjected to incomplete oxidation with chromic acid mixture, it yields a solid and a liquid phenyl-tolyl ketone, $C^6H^5.CO.C^6H^4.CH^3$, the former convertible by further oxidation into parabenzoylbenzoic acid, $C^6H^5.CO.C^6H^4.COOH$, in which $CO.C^6H^5 : COOH = 1 : 4$, the latter into a mixture of meta- and ortho-benzoylbenzoic acids. The crude benzyl-toluene is therefore a mixture of three isomeric compounds, in which the radicles $CH^2.C^6H^5$ (benzyl) and CH^3 stand to one another in the relative positions 1 : 4, 1 : 3, and 1 : 2.

The three benzyl-toluenes have not been directly separated one from the other, but the *para*-modification is obtained by distilling solid tolyl-phenyl-ketone with zinc dust. It boils at 279° – 280° (corr. 285° – 286°), remains fluid in a mixture of ice and salt, and is oxidised by chromic acid mixture to parabenzoylbenzoic acid. When passed in the state of vapour through a tube filled with pumice and heated to low redness, it remains unaltered, whereas the mixture of the three benzyl-toluenes yields thereby a large quantity of anthracene (Behr a. van Dorp, *Ber.* vii. 18). The same hydrocarbon is abundantly formed when crude benzyl-toluene is heated with lead oxide, its production in both cases being probably due to the ortho-benzyltoluene contained in the mixture (Behr a. van Dorp, *ibid.* vi. 753). According to Barbier (*Jahresb. f. Chem.* 1873, 359), benzyl-toluene is decomposed by the action of heat alone into anthracene, toluene, and free hydrogen:



The anthracene thus produced forms brown laminae with Fritzsche's reagent, whence it appears to contain phenanthrene (q. v.)

* The compounds here called *methylene-diphenylenes* have hitherto been known as diphenylene-methanes (p. 670); but this name belongs more properly to the compound $C^6H^5 \equiv C \equiv C^6H^5$, which has not yet been obtained.

Methylene-diphenylenes.

	<i>α</i> -Methylene-diphenylene from diphenylmethane and diphenylene ketone (Graebe, Fittig, and Schmitz)	<i>β</i> -Methylene-diphenylene fluorene (Berthelot; Barbier)	<i>γ</i> -Methylene-diphenylene From benzene and toluene (Carnelley)	<i>δ</i> -Methylene-diphenylene
Melting point	115°-114° (Graebe), 112°-113° (Fittig a. Schmitz).	113°	118° (uncorr.)	205° (uncorr.), 208° (corr.)
Boiling point	300°-305° (Graebe); 294°-295° (Fittig a. Schmitz).	About 305° (corr.)	285° (uncorr.)	About 230°.
Crystalline form	Colourless laminae with faint blue fluorescence.	Sublimes in plates with strong violet fluorescence.	Colourless pearly plates or small needle-shaped prisms, with very faint blue fluorescence.	Small colourless pearly plates.
Solubility	Easily in hot alcohol. Less soluble in cold alcohol, very easily in carbon bisulphide, ether, and benzene.	Very soluble in ether, benzene, carbon bisulphide, and hot alcohol, but only sparingly soluble in cold alcohol.	Moderately soluble in hot alcohol or hot glacial acetic acid, but only sparingly soluble in cold alcohol or cold glacial acetic acid; easily in ether.	Sparingly soluble in cold, but more easily in hot alcohol.
Picrate	Yellow-red or red needles, m. p. = 80°-82°, very easily soluble in alcohol, but decomposed at same time (Graebe). Red-brown prisms, m. p. = 79°-80° (Fittig a. Schmitz).	Red needles, m. p. 80°-82°.	Black-red needles, m. p. = 79°-81°.	—
Dibromo-compound	Colourless tabular monoclinic prisms, different in form from those of Barbier; m. p. = 162°-167° (Fittig a. Schmitz). Needles, m. p. 153°-154° (Graebe). Very sparingly soluble in alcohol, very easily in ether, benzene, carbon bisulphide, and chloroform.	Monoclinic crystals, m. p. = 168°-167°. Nearly insoluble in ether and alcohol, but readily soluble in carbon bisulphide and chloroform. They change on repeated crystallisation from carbon bisulphide into the same form as those of Fittig a. Schmitz.	Minute octohedrons or needles, the latter changing into the former. M. p. = 162°. Very sparingly soluble in alcohol or ether, whether hot or cold.	—
Dinitro-compound	Colourless needles, m. p. 199°-201°, very slightly soluble in hot alcohol.	Reddish yellow needles, m. p. = above 260° with decomposition, very slightly soluble in ordinary solvents.	—	—
Oxidation-products	Is oxidised with difficulty, and gives only diphenylene ketone.	Is slowly oxidised, giving diphenylene ketone and a quinone, C ¹⁰ H ⁶ O ₂ , m. p. = 181°-182°.	Gives only a quinone and no ketone. The quinone, C ¹⁰ H ⁶ O ₂ , crystallises in golden-yellow needles, m. p. = 280°-281°. Scarcely soluble in cold, and only sparingly soluble in hot alcohol.	Gives only a quinone and no ketone. The quinone, C ¹⁰ H ⁶ O ₂ , is a pure white powder, subliming in needles (m. p. 288°). Insoluble in water, but moderately soluble in glacial acetic acid.

The *dinitrobenzyl-toluene* (m. p. 137°) which Zincke a. Milne obtained by treating crude benzyl-toluene with strong nitric acid (vii. 183), appears from experiments by Plascuda a. Zincke (*Deut. Chem. Ges. Ber.* vii. 982) to be derived from parabenzyl-toluene. Another dinitrobenzyl-toluene is formed at the same time, probably derived from ortho-benzyl-toluene; it crystallises in small concentrically-grouped needles, and melts at 100°.

Dibenzyl-toluenes, $C^{12}H^{20} = CH^3.C^6H^5(CH^2.C^6H^5)^2$.—The crude product remaining after the monobenzyl-toluene has been distilled off is a thick brownish oil, which begins to boil at 320°, and may be completely distilled between 450° and 500°, leaving only a small quantity of tarry residue.

The portion distilling between 320° and 380° may be separated by a series of fractional distillations into anthracene and a liquid product consisting chiefly of monobenzyl-toluene.

The portion distilling between 380° and 420° yields by further fractionation a large quantity of an oily, slightly aromatic, fluorescent liquid, having the composition of dibenzyl-toluene. This hydrocarbon boils at 392°–396° under ordinary pressure, at about 280°–285° under a pressure of 30–40 mm., and has a specific gravity of 1.049. It dissolves easily in alcohol, ether, chloroform, and benzene, does not combine with picric acid, and is converted by nitric acid into resinous nitro-products not admitting of purification. When passed in the state of vapour through a red-hot tube, it splits up into hydrogen, toluene, anthracene, and an isomeride of the latter. By oxidation it yields two isomeric dibenzoylbenzoic acids, $C^{12}H^{14}O^4$ (p. 309), and a third infusible acid having the composition $C^{13}H^{10}O^5$, or probably $C^6H^5-CO-C^6H^5(COOH)^2$. This acid may be formed from one of the dibenzoylbenzoic acids by abstraction of C^6H^5 , or it may be derived from a distinct modification of the hydrocarbon $C^{12}H^{20}$. From this it may be inferred that the dibenzyl-toluene obtained as above is a mixture of two, if not of three, isomeric hydrocarbons.

The oxidation of dibenzyl-toluene likewise yields a considerable quantity of ketones, and by further decomposition, carbonic, acetic, and benzoic acids. The attempt to separate these ketones was not successful, but yielded a viscid honey-yellow mass having the composition $C^{21}H^{16}O^2$, easily soluble in alcohol and ether, distilling unaltered at 300°–305° under a pressure of 30–40 mm., but decomposing when repeatedly distilled under ordinary pressure, and yielding thereby—together with small quantities of water, toluene, benzaldehyde and anthraquinone—a large quantity of anthracene, and an isomeric hydrocarbon differing from phenanthrene, and identical with the one already mentioned, as resulting from the decomposition of benzyl-toluene by heat (see ANTHRACENE, p. 95).

The portion of the crude product of the action of benzyl chloride on toluene in presence of zinc which boils above 420°, yields by further fractionation anthracene and toluene, the formation of which, as well as of the anthracene occurring in the lower-boiling portions, is attributed by Weber a. Zincke to the splitting-up of hydrocarbons having the composition nC^7H^8 , which may be supposed to be formed from nC^7H^7Cl by elimination of $nHCl$. More highly benzylated tolueues are doubtless also present.

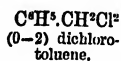
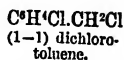
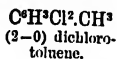
11. A mixture of toluene and benzoyl chloride, $C^6H^5.CO.Cl$, is decomposed by zinc with evolution of hydrogen chlorides, but the greater part of the benzoyl chloride is decomposed in the same manner as it would be if heated alone (Zincke, *Ber.* vii. 137).

12. *Action of Phosphorus Pentoxide on a mixture of Toluene and Fluorenic Alcohol.* When P_2O^5 (12 g.) is heated for four or five hours in a sealed tube at 140°–150° with a saturated solution of fluorenic alcohol (10 g.) in toluene, the product washed with water, the excess of toluene expelled by a gentle heat, the residual liquid distilled, and the solidified distillate recrystallised, from boiling glacial acetic acid, diphenylene-tolyl-methane, $(C^6H^5)^2=CH.C^6H^4.CH^3$, is obtained in long, slender, silky, lustrous needles melting at 128°, slightly soluble in alcohol and ether, freely in benzene and in hot water; it does not combine with picric acid (Hemilian, *Ber.* xi. 202).

Substitution-derivatives of Toluene.

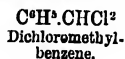
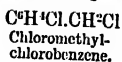
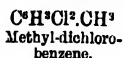
The substitution of chlorine, bromine, nitryl, &c. for an equivalent quantity of hydrogen in toluene may take place either in the C^6H^5 -group or in the CH^3 -group (v. 852). The derivatives of the former class have hitherto been designated as chloro-, bromo-, nitro-toluenes, &c., those of the latter as chlorides, bromides, &c. of benzyl, benzylene, or benzenyl, e.g. $C^6H^5.CH^2Cl$, benzyl chloride; $C^6H^5.CHCl^2$, benzylene dichloride; $C^6H^5.CCl^3$, benzenyl trichloride. Another mode of distinction has been proposed by Beilstein a. Kuhlberg, consisting in placing before the name of the compound the number of the hydrogen-atoms displaced by chlorine, &c., either in the

C^6H^3 -group, or in the CH^3 -group, or in both. Thus the three known dichlorotoluenes may be named as follows:



In speaking of those of the first class, however, in which the substitution takes place wholly in the C^6H^3 -group, the numerical prefix may in most cases be dispensed with, the compounds in question being designated simply as chloro-, bromo-toluenes, &c.

The three chlorotoluenes may also be designated systematically as follows:



BROMOTOLUENES.

(1-0) **Monobromotoluenes**, $C^6H^4Br.CH^3$. Körner (*Gazz. chim. ital.* 1874) prepares *orthobromotoluene* from orthotoluidine (b. p. 199.5°-196.6°) by converting the nitrite of this base into the diazoperbromide, and decomposing the latter with alcohol. The product, freed from the greater part of the alcohol by slow distillation, is washed with potash-solution, distilled with steam, dried, and fractionated. It boils at 182°, and smells like orthodibromobenzene. By oxidation with dilute nitric acid (instead of chromic acid) it is easily converted into *o*-bromobenzoic acid (Zincke, *Ber.* vii. 143). *Metabromotoluene* was prepared from *p*-nitrotoluene, by successive conversion into *p*-toluidide, acetotoluide, bromacetotoluide, bromotoluidine, $[CH^3 : Br : NH^2 = 1 : 3 : 4]$, the nitrate of this base, the diazoperbromide, and finally into $[1 : 3]$ bromotoluene. This compound, after drying with phosphoric anhydride, boils at 184°-184.1° [bar. 754.1 mm.] Another preparation boiled at 184.3° [bar. 758.74]. Its odour is undistinguishable from that of metadibromobenzene. By oxidation it is converted into metabromobenzoic acid, melting at 154°. *Parabromotoluene* is formed, together with the other two modifications and benzyl bromide, by direct bromination of toluene; also from *p*-toluidine by substitution of bromine for NH^2 . After drying with phosphoric anhydride, it melts at 282°, resolidifies at 25.4°, and boils at 184.6° (bar. 760.74); smells very much like *p*-dibromobenzene (Körner).

(2-0) **Dibromotoluenes**, $C^6H^3Br^2.CH^3$. The six possible dibromotoluenes are obtained either by direct bromination of the monobromotoluenes, or by converting the monobromotoluidines into diazoperbromides, and decomposing these compounds by boiling with alcohol. Their formation by this latter process throws considerable light on the influence of the amido-group, NH^2 , in determining the position taken up by bromine (or other halogen) when it enters into a compound already containing the amido-group; and with this view they have lately been especially studied by Neville a. Winther (*Chem. Soc. J.* 1880, xxxvii. 429-453). With regard to this influence, Körner, in his classical research, 'On the Isomerism of the Aromatic Compounds containing six atoms of Carbon' (*Gazz. chim. ital.* 1874, 305; see also p. 161 of this volume), laid down the rule that when a halogen-element, or the nitro-group NO^2 , is introduced into aniline, it takes up the para-position with respect to the NH^2 -group; and Neville a. Winther, in the paper just referred to, have shown that this rule is of more general application, and that when bromine, or other halogen-element, or the nitro-group, is directly introduced into toluidine, as well as into aniline, it takes up the para-position with regard to the amido-group—or if this position is already occupied by any other groups or radicles, that the halogen then takes up one of the two ortho-positions, but that it cannot under any circumstances be made to take up a position meta to the amido-group. Wroblewsky, who prepared five out of the six dibromotoluenes from the corresponding monobromotoluidines by the diazoperbromide reaction (vii. 1165), obtained results which were in some cases inconsistent with Körner's rule, but the experiments of Neville a. Winther tend, as above said, to show that the rule holds good in every case. The following are the results of these experiments:

(1 and 2). *Ortho-meta-dibromotoluenes*, $CH^3 : Br : Br = 1 : 2 : 3$ and $1 : 2 : 5$. The latter of these modifications is obtained from orthobromo-metatoluidine, and from metabromo-orthotoluidine by the diazo-reaction as follows: Acetorthotoluide, treated with 1 mol. bromine, gives a monobromacetotoluide, and this by decomposition with potash gives a monobromotoluidine, which, after separation from small quantities of dibromotoluidine formed at the same time, by solution in dilute hydrochloric acid, precipitation with sodium carbonate, and distillation with steam, melts at 55°-56°

(Wroblewsky gives 58°). The diazo-perbromide of this monobromotoluidine decomposed by warming it with glacial acetic acid yields the dibromotoluene. The acetyl derivative of meta-toluidine, subjected to the same series of reactions, yields a dibromotoluene which was regarded by Wroblewsky as different from that obtained from orthotoluidine. Neville a. Winther, on the other hand, find that the two products thus obtained are identical; they are both fluid at ordinary temperatures, and do not solidify in a mixture of ice and salt; their nitro-derivatives, obtained by treating them with fuming nitric acid, melt at nearly the same temperature (87.6° – 88.6°), and the corresponding amido-compounds at 84° – 85.1° .

This dibromotoluene being obtained either from *m*-brom-*o*-toluidine or from *o*-brom-*m*-toluidine, must be an ortho-meta-derivative, viz. either 1 : 2 : 5 or 1 : 2 : 3; and hence also it may be inferred that when bromine is introduced into orthotoluidine, it takes the meta-position relatively to CH_3 , and that when introduced into meta-toluidine it takes the ortho-position. The mode of formation does not afford the means of deciding by which of the two formulæ the constitution of the dibromotoluene is represented, in other words whether the two bromine-atoms are ortho- or para- to each other; but an *o*-*m*-dibromotoluene different from it may be obtained by the following process:—

By adding an aqueous solution of bromine (rather more than 1 mol.) to *m*-nitro-*o*-toluidine suspended in water, a bromonitro-ortho-toluidine, $\text{C}_6\text{H}_4(\text{NH}_2)\text{Br}(\text{NO}_2)$, is obtained, which, when purified by recrystallisation from alcohol, melts at 180.3° – 181.3° (corr.) To determine the constitution of this bromonitrotoluidine, Neville a. Winther further prepared the isomeric compound (m. p. 139°) which Wroblewsky obtained by nitrating *m*-brom-*o*-acetoluide, and taking out the acetyl-group; they also prepared bromonitroparatoluidine in two ways, viz., (a) by first nitrating and then brominating, and (B) by first brominating and then nitrating. The four products thus obtained were treated with nitrous gas and alcohol to remove the amido-group, and the resulting bromonitrotoluene was reduced with tin and hydrochloric acid. The bromotoluidine thus produced was also converted into an aceto-compound by boiling with glacial acetic acid for seven or eight hours.

The results are given in the following table:—

	From <i>o</i> -toluidine by first nitrating and then brominating	From <i>o</i> -toluidine by first brom- inating and then nitrating	From <i>p</i> -toluidine by first nitrating and then brominating	From <i>p</i> -toluidine by first brom- inating and then nitrating
Nitrobromotoluidine . .	m. p. 180.3° – 181.3°	m. p. 143.0°	m. p. 64° – 65°	m. p. unpurified, 63°
Nitrobromotoluene . .	81.4° – 81.8°	81.4° – 81.8°	81.4° – 81.8°	81° – 81.5°
Bromotoluidine . .	35.6° – 36°	34.5° – 37°	36.6°	35° – 35.2°
Aceto-compound of the bromotoluidine. .	167° – 168°	167° – 168°	167° – 168°	168°

Hence it appears that the bromonitrotoluenes obtained by the four methods above described are identical. The bromotoluidines obtained from them differ slightly in melting point, but not sufficiently to indicate any difference in constitution between the several products. Now it has been shown above that bromine when introduced into orthotoluidine takes up the *meta*-position relatively to the methyl-group, and it is known that the NO_2 -group also takes up the *m*-position relatively to CH_3 in both *o*- and *p*-toluidine. Hence the bromonitrotoluene obtained as above must have the symmetrical constitution 1 : 3 : 5, and it may also be seen that bromine when introduced into paratoluidine takes up the meta-position with regard to CH_3 .

It follows therefore that of the first two bromonitrotoluidines, one must have the constitution $\text{CH}_3 : \text{NH}_2 : \text{Br} : \text{NO}_2 = 1 : 2 : 3 : 5$, and the other $\text{CH}_3 : \text{NH}_2 : \text{NO}_2 : \text{Br} = 1 : 2 : 3 : 5$. Further, on decomposing the diazoperbromide of *m*-bromo-*m*-nitro-*o*-toluidine by heating it with glacial acetic acid, a dibromonitrotoluene was obtained melting at 105.4° ; and on reducing this with iron and acetic acid, and distilling the separated base with steam, a dibromotoluidine was formed which melted at 86.4° , and when heated with nitrous gas and alcohol to remove the amido-group, yielded a dibromotoluene which after distillation with steam melted at 27.4° – 27.8° , and was

converted by strong nitric acid into a nitro-compound melting at 51° – 62° . The same dibromotoluene was obtained from the above-mentioned aceto-*m*-bromo-*m*-toluide melting at 167° – 168° . This compound, treated with a molecular proportion of bromine in aqueous solution, heat being applied towards the end to complete the absorption, yielded a dibromacetoluide melting at 204° – 205° . On heating this last body with a mixture of hydrogen sulphate and water in equal volumes, then diluting the liquid with water, and cooling, the sulphate of a dibromotoluidine crystallised out, and this salt decomposed with sodium carbonate, yielded a dibromotoluidine melting, after recrystallisation from alcohol, at 83° – 85° . Lastly, on decomposing this base with nitrous gas and alcohol, and distilling with steam, a dibromotoluene was obtained which melted at 27.4° – 28° , and yielded a nitro-compound melting at 56.5° – 57.5° , so that it may be regarded as identical with the dibromotoluene last described.

To decide the question as to which of the two dibromotoluenes obtained as above has the composition 1 : 2 : 5, and which is 1 : 2 : 3, they were converted into dibromobenzoic acids by heating them with dilute nitric acid (1 vol. acid of sp. gr. 1.36 to three of water) for about three days. In this way the fluid dibromotoluene prepared from ortho- and from meta-toluidine was converted into a dibromobenzoic acid melting at 149° – 153° , and yielding on distillation with lime paradibromobenzene melting at 85° – 86° (m. p. of pure *p*-dibromobenzene 89°).

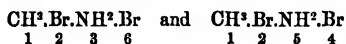
Hence this dibromotoluene has its two bromine atoms in the para-position with regard to each other, and is therefore the 1 : 2 : 5 modification, $C^6H^3Br_2.H.Br.H.Br.H$, and consequently the other *o*-*m*-modification melting at 27.4° – 27.8° , prepared from *m*-nitro-*o*-toluidine, has the constitution 1 : 2 : 3 or $C^6H^3Br.Br.Br.H$.

(3). *Symmetrical* or *m-m-Dibromotoluene*, $CH^3 : Br : Br = 1 : 3 : 5$. Wroblewsky obtained this modification only from dibromorthotoluidine; Neville & Winther have obtained it also from dibromoparatoluidine. Orthotoluidine in alcoholic, or in acid aqueous solution treated with a slight excess of bromine, yields (after precipitation with water in the former case, and after distillation with steam) a white crystalline dibromotoluidine melting at 43° – 45° , while paratoluidine similarly treated yields a dibromo-derivative melting at 73° . When these dibromotoluidines were treated with an alcoholic solution of nitrous acid, the first gave after distillation with steam a dibromotoluene melting at 39° ; the second a product which generally melted a little higher, but was easily separated by recrystallisation into two substances, one of which melted at 39° , and was to all appearance identical with the dibromotoluene just described, while the other, obtained only in very small quantity, appeared to be a bye-product of the action of the nitrous gas, perhaps an amidazo-compound. The dibromotoluene melting at 39° gave on treatment with fuming nitric acid, a nitro-compound which at first melted at 120° – 125° , but separated on repeated crystallisation into two dibromodinitrotoluenes, one melting at 157.6° – 158.3° , the other at 105° ; and the same dibromotoluene when oxidised with a mixture of chromic and acetic acids was converted into symmetrical dibromobenzoic acid, $[CO^2H : Br : Br = 1 : 3 : 5]$, melting between 207° and 210° (p. 261): hence this dibromotoluene must also be symmetrically constituted, that is, must be represented by the formula $C^6H^3.H.Br.II.Br.H$.

(4). *Meta-para-dibromotoluene* [1 : 3 : 4] is prepared by the diazo-perbromide reaction from monobromoparatoluidine. It is liquid at ordinary temperatures, as observed by Wroblewsky, gives a crystalline nitro-derivative melting at 86.6° – 87.5° , and convertible by reduction with iron and acetic acid into an amido-derivative melting at 96.8° – 98° . By oxidation with chromic and acetic acid, this dibromotoluene is converted into a dibromobenzoic acid melting at 232° – 233° , agreeing therefore very nearly with the [1 : 3 : 4] dibromobenzoic acid described by Burghardt, which melted at 227° – 230° (p. 361): hence the constitution of the dibromotoluene is established.

(5 and 6). *Ortho-para-* and *Ortho-ortho-dibromotoluenes*, 1 : 2 : 4 and 1 : 2 : 6.—When the aceto-compound of *o*-etoluidine is treated with 2 mol. bromine, the first molecule is readily absorbed, forming a monobromaceto-compound, but the second is absorbed much more slowly, giving at last a dibromaceto-compound which, on the removal of the acetyl-group with alcoholic potash, gives a mixture of two dibromotoluidines, together with a small quantity of tribromotoluidine. The di- and tribromo-compounds may be separated from monobromotoluidine formed at the same time by distillation from dilute acid, which retains the latter, and then extracted with hot strong hydrochloric acid, the liquid on cooling depositing crystals consisting of a mixture of di- and tribromotoluidine. The portion which had remained undissolved in the hydrochloric acid was repeatedly distilled with steam, the last portions being rejected, and the distillate thus purified was recrystallised from alcohol, whereby a portion (the largest by far) was obtained, melting at 74.6° – 75.3° . This appeared to consist of a single dibromotoluidine, and the mother-liquors contained another dibromotoluidine melting at a lower temperature, viz. 33° – 35° . Now, according to the

theory already explained respecting the orientation of Br with respect to the NH_2 -group, metatoluidine should yield two different dibromo-derivatives, viz.:



and these, on removal of the amido-group, should yield the two dibromotoluenes 1 : 2 : 6 and 1 : 2 : 4. The dibromotoluene obtained from the first (m. p. 74.6° – 75.3°) is an oil which remains liquid at -20° , and gives on nitration at ordinary temperatures a mixture of nitro-compounds separable by crystallisation from alcohol into a mononitrodibromotoluene which crystallises in white needles melting at 80° – 80.6° , and a mixture of di- and trinitrodibromotoluenes melting at 128° – 129° . The same dibromotoluene, treated with dilute nitric acid, yields a dibromobenzoic acid melting at 167° – 169° . The dibromotoluene obtained from the dibromotoluidine melting at 33° – 35° is also an oil which does not solidify at -20° , and gives on nitration a mixture separable by recrystallisation from alcohol into a compound melting at 159° – 161° , and only moderately soluble in alcohol, from which it crystallises in long slender needles; also another in small quantity, melting below 80° . This dibromotoluene, heated with nitric acid, yielded a dibromobenzoic acid melting at 150° – 167° .

The behaviour of these two dibromotoluenes with fuming nitric acid shows that they are different from any of the four above described, and therefore that their constitutions must be 1 : 2 : 4 and 1 : 2 : 6 respectively. To decide which of the two must be represented by the former and which by the latter, they were prepared in other ways.

To obtain the 1 : 2 : 4 modification, ordinary dinitrotoluene (m. p. 70°), which is known to have this constitution, was converted by reduction with alcoholic ammonium sulphide into orthonitroparatoluidine (m. p. 77° – 78°); this by the diazoperbromide reaction into *o*-nitro-*p*-bromotoluene (large monoclinic tables melting at 44.4° – 45.2°), which on reduction gave *p*-brom-*o*-toluidine, $\text{C}^6\text{H}^3\text{NH}^2\text{H.Br.H.H}$, and this base was converted by the diazoperbromide reaction into 1 : 2 : 4 dibromotoluene, which was thus obtained is an oil not solidifying at -20° , convertible by fuming nitric acid into a mononitro-derivative melting at 80.5° – 81.3° , and by oxidation with dilute nitric acid into a dibromobenzoic acid melting at 168° – 170° . These results show that the dibromotoluene obtained from the dibromometatoluidine which melts at 78° – 84° (*supra*) has also the constitution 1 : 2 : 4. Hence it follows that the dibromotoluene prepared from the dibromotoluidine melting at 33° – 35° must have the constitution 1 : 2 : 6; and this conclusion has been confirmed by a special mode of preparing this last modification for which reference must be made to Neville a. Winther's paper (p. 444).

(1–1). *Dibromotoluene*, or *Bromomethyl-bromobenzene*, $\text{C}^6\text{H}^4\text{Br.CH}^2\text{Br}$, syn. with Bromobenzyl Bromide (see p. 314).

(3–0). **Tribromotoluenes**, $\text{C}^6\text{H}^3\text{Br}^3\text{CH}^3$ (Neville a. Winther, *Chem. Soc. J.* xxxvii. 446). (1). $\text{C}^6\text{H}^3\text{Br}^3\text{Br.H.Br.H}$, prepared from the diazoperbromide of dibromorthotoluidine, crystallises in long flat colourless needles melting at 52° – 53° . By dissolution in nitric acid of sp. gr. 1.52, and precipitation with water, it is converted into a nitro-derivative which, after crystallisation from alcohol, melts at 95° – 170° .

(2). $\text{C}^6\text{H}^3\text{H.Br.Br.Br.H}$, prepared from the diazoperbromide of dibromoparatoluidine, melts at 88° – 89° .

(3). $\text{C}^6\text{H}^3\text{H.Br.Br.H.Br}$ is prepared from the diazoperbromide of the dibromometatoluidine melting at 74° – 75.5° , which has already been shown to have the constitution $\text{C}^6\text{H}^3\text{H.NH}^2\text{Br.H.Br}$ (*supra*). It crystallises from alcohol in long colourless shining needles melting at 111.2° – 112.8° .

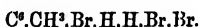
(4). $\text{C}^6\text{H}^3\text{Br}^3\text{Br.Br.H.H}$ was prepared by converting *m*-bromo-*m*-nitro-*p*-toluidine into the diazoperbromide; this into *m*-bromo-*m*-nitro-*p*-bromotoluene,



(colourless laminæ melting at 62° – 63.6°); reducing this latter with iron and acetic acid, whereby a dibromotoluidine was obtained, which crystallised from alcohol in long colourless needles or flat prisms melting at 58° – 59° ; converting this amido-compound into the corresponding aceto-derivative (m. p. 162° – 163°) by boiling it for twenty-four hours with the strongest glacial acetic acid; suspending this aceto-compound in water, and treating it with bromine, whereby a tribromacetoluide was obtained, crystallising from alcohol in white needles melting at 171° – 173° ; decomposing this compound with alcoholic potash; and treating the resulting tribromotoluidine (m. p. 96° – 96.8°) with nitrous acid and alcohol. In this manner a tribromotoluene was finally obtained, melting at 44.4° – 44.7° . By treating it with nitric acid of sp. gr.

1.52 and precipitating with water, a nitro-compound was formed, which, after frequent recrystallisation, melted at about 106° – 107° . This result sufficiently distinguishes the tribromotoluene under consideration from the first-described modification (m. p. 52° – 53°), which gives a nitro-compound melting at 95° – 170° .

(5). $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{H}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}$. This modification was obtained by Wroblewsky from bromo-nitro-orthotoluidine melting at 143° —which has already been shown to have the constitution $\text{C}^6\text{H}^3\text{NH}^2\text{NO}^2\text{H}^{\cdot}\text{Br}^{\cdot}\text{H}^{\cdot}$ (p. 1988)—by converting it, through the diazoperbromide reaction, into a dibromonitrotoluene melting at 69.5° – 70.2° ; and proceeding, as in the last case, by the successive employment of tin and hydrochloric acid, glacial acetic acid, bromine, and boiling alcoholic potash, whereby ultimately a tribromotoluidine is obtained which melts at 93° – 94° , and, when treated with nitrous gas and alcohol, yields a tribromotoluene crystallising in flat needles which melt at 58° – 59° . Now the mode of formation of this tribromotoluene shows that it must be represented by one of the two formulæ:



But the former of these belongs to the modification (m. p. 111.2°) obtained from dibromometatoluidine perbromide: hence the modification under consideration must be represented by the latter formula. This tribromotoluene is converted by nitric acid of sp. gr. 1.52 into a nitro-compound melting, after recrystallisation, at 91° – 91.4° .

(6). $\text{C}^6\text{H}^3\text{Br}^3\text{H}^{\cdot}\text{Br}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}$. This modification was prepared in like manner from the tribromometatoluidine which melts at 100° – 101.6° . Now this tribromotoluidine can be obtained by bromination of dibromometatoluidine, $\text{C}^6\text{H}^3\text{Br}^2\text{H}^{\cdot}\text{Br}^{\cdot}\text{NH}^2\text{H}^{\cdot}$ (p. 1990), and must therefore be represented either by the formula $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{Br}^{\cdot}\text{NH}^2\text{H}^{\cdot}$ or by $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}\text{NH}^2\text{Br}^{\cdot}$. It cannot, however, be represented by the first of these formulæ, since, when decomposed by alcohol and nitrous gas, it gives a tribromotoluene which melts at 66° , whereas it has been already shown (p. 1990) that the tribromotoluene derived from this base melts at 44.4° . The dibromotoluidine in question must therefore be represented by the second of the above formulæ, and the tribromotoluene derived from it by the formula $\text{C}^6\text{H}^3\text{Br}^3\text{H}^{\cdot}\text{Br}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}$.

(4–0). **Tetrabromotoluenes**, $\text{C}^6\text{HBr}^4\text{CH}^3$. Of these there are three possible modifications:

(1). $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{Br}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}$ is prepared from tetrabromometatoluidine (which is obtained by the action of bromine-water on a solution of *m*-bromo-*m*-toluidine, m. p. 35° – 37° , in hydrochloric acid, and crystallises in white needles melting at 223° – 224°) by boiling with alcohol and nitrous gas; also from tribromometatoluidine perbromide. The product obtained by the first process melts at 105° – 108° , that by the second at 106.8° – 108° . By nitration with nitric acid of sp. gr. 1.52, it yields a nitro-compound melting at 215° – 216° .

(2). $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{H}^{\cdot}\text{Br}^{\cdot}\text{Br}^{\cdot}$ is obtained by the diazoperbromide reaction from tribromometatoluidine, $\text{C}^6\text{H}^3\text{Br}^3\text{Br}^{\cdot}\text{H}^{\cdot}\text{NH}^2\text{Br}^{\cdot}$ (m. p. 93° – 94°) described above. It melts at 116° – 117° , and yields a nitro-compound melting, after recrystallisation from alcohol, at 213° .

(3). $\text{C}^6\text{H}^3\text{Br}^3\text{H}^{\cdot}\text{Br}^{\cdot}\text{Br}^{\cdot}\text{Br}^{\cdot}$ is obtained from tribromometatoluidine,



(m. p. 96° – 96.8°), described on p. 1990. It melts at 111° – 111.5° , and gives a nitro-compound melting at 212° .

(5–0). **Pentabromotoluene**, $\text{C}^6\text{Br}^5\text{CH}^3$, is obtained from the diazoperbromide of tetrabromotoluidine (m. p. 223° – 224°), and purified by crystallisation from acetic acid or alcohol, neither of which dissolves it freely; it crystallises in white needles melting at 283° – 285° (Neville a. Winther). It is also produced by adding toluene to an excess of bromine mixed with aluminium bromide in a cooled vessel (Gustavson, *Ber.* x. 971).

The table on p. 1992 exhibits a comparative view of the constitution and distinguishing properties of the several bromotoluenes.

Chlorotoluenes. (1–0). *Monochlorotoluenes*, $\text{C}^6\text{H}^4\text{ClCH}^3$.—The *para*-modification, already described (v. 853), may be prepared from solid nitrotoluene by reducing that compound with tin and hydrochloric acid, drenching the hydrochloride of the resulting amidotoluene with fuming hydrochloric acid, passing nitrous gas into the pasty mass till it assumes a yellow-brown colour and the crystals are completely dissolved, and boiling the liquid in a vessel provided with a condensing tube. Nitrogen is then given off, and the acid and aqueous vapours which distil over are accompanied by an oil containing the monochlorotoluene, together with cresol, nitrocresol, and nitrotoluene. To obtain the chlorotoluene pure, the entire product is

BROMOTOLUENES [CH³ in position 1]

2	3	4	5	6	Fluid, b. p. 182°-183° Fluid, b. p. 184° M. p. 28.5°; b. p. 185° Fluid M. p. 27.4°-27.8° M. p. 39° Fluid Fluid Fluid M. p. 52°-53° " 88°-89° " 111°-112° " 44.4°-44.7° " 58°-59° " 66° " 106.8°-108° " 116°-117° " 111°-111.5° " 283°-285°	Product of nitration with HNO ₃ , sp. gr. 1.52	Reduction- product of nitro-compound	Dibromobenzoic acid
Br	—	—	—	—	Fluid, b. p. 182°-183°	See v. 853; vi. 279-281; vii. 1164-1165		
—	Br	—	—	—	Fluid, b. p. 184°			
—	—	Br	—	—	M. p. 28.5°; b. p. 185°			
Br	—	—	Br	—	Fluid	Mononitro, 88°-89°	84°-85°	With HNO ₃ , 151°-153°
Br	Br	—	—	—	M. p. 27.4°-27.8°	Mononitro, 56.5°-57.5°	52°-53°	With HNO ₃ , 147°-149°
—	Br	—	Br	—	M. p. 39°	Two dinitro, 157.5°-158° and 105°	—	With CrO ₃ , 208°-210°
—	Br	Br	—	—	Fluid	Mononitro, 86.6°-87.5°	97°-98°	With CrO ₃ , 232°-233°
Br	—	Br	—	—	Fluid	Mononitro, 80°-81°, and others	—	With HNO ₃ , 168°-170°
Br	—	—	—	Br	Fluid	Dinitro, 161.6°-162.2°		
Br	Br	—	Br	—	M. p. 52°-53°	—		
—	Br	—	Br	—	" 88°-89°	—		
Br	—	Br	Br	—	" 111°-112°	—		
Br	Br	Br	—	—	" 44.4°-44.7°	M. p. 106°-107°		
Br	Br	—	—	Br	" 58°-59°	" 91°-91.4°		
Br	—	Br	—	Br	" 66°	" 217°-220°, dinitro		
Br	Br	Br	—	Br	" 106.8°-108°	" 215°-216°		
Br	Br	—	Br	Br	" 116°-117°	" 213°		
—	Br	Br	Br	Br	" 111°-111.5°	" 212°		
Br	Br	Br	Br	Br	" 283°-285°			

treated with tin and hydrochloric acid, then distilled with water, shaken with soda-ley, and again distilled with water. The chlorotoluene thus obtained boils at 150.5° , and solidifies on cooling to about 0° to a colourless laminar mass which melts at 6.5° (Hübner a. Majert, *Ber.* vi. 794).

Parachlorotoluene is also formed by passing chlorine into a mixture of anhydrous toluene and molybdenum pentachloride heated on the water-bath. The action goes on regularly, and soon after 1 equiv. of chlorine has been taken up, the product is found to consist almost wholly of parachlorotoluene boiling at 158° – 161° , and having a density of 1.0735 at 27.2° (ρ 17.2°). *Orthochlorotoluene* (b. p. 156°) obtained by Griess's reaction from chlorinated orthotoluidine has been already described (vi. 281). *Metachlorotoluene*, prepared in like manner from metachloroparatoluidine, $C^6H^3H.Cl.NH^2.H.H$, is a liquid which boils at 156° , and is converted by oxidation into metachlorobenzoic acid (Wroblewsky, *Liebig's Annalen*, clxviii. 199).

(0–1) *Chlorotoluene, Chloromethylbenzene, or Benzyl Chloride*, $C^6H^5.CH^2Cl$.—The preparation of this compound by the action of chlorine on heated toluene, and by that of hydrochloric acid on benzyl alcohol, has already been described; also several of its reactions (see v. 854; vii. 179; viii. 314). On the products obtained by heating it with finely divided zinc and hydrocarbons of the benzene series, see vii. 183; viii. 315.

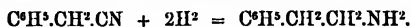
The action of benzyl chloride on nitrite of silver or potassium does not yield any aromatic nitro-compound, the product consisting of high-boiling non-nitrogenous bodies amongst which are found anthracene, benzoic acid, and benzaldehyde (H. Brunner, *Ber.* ix. 1744).

(2–0) *Dichlorotoluene*, $C^6H^4Cl^2.CH^3$, is formed by the continued action of chlorine on toluene mixed with molybdic chloride. When purified by continued fractionation, it has a density of 1.2596 at 18.4° , and 1.2518 at 16° ; boils at 196° – 198° . The product thus obtained is, however, a mixture of two isomeric bodies, inasmuch as when oxidised by chromic acid mixture it yields two dichlorobenzoic acids (Aronheim a. Dietrich, *Ber.* viii. 1401).

(0–2) *Dichlorotoluene, Dichloromethylbenzene, or Benzylene Dichloride*, $C^6H^4.ClHCl^2$ (see p. 320).

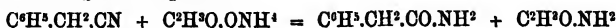
Trichlorotoluenes, $C^6H^3Cl^3$. See vi. 281–2. Aronheim a. Dietrich (*Ber.* viii. 1401), by the action of chlorine on a mixture of toluene and molybdic chloride, have obtained, besides the solid (3–0) trichlorotoluene melting at about 75° (vi. 282), a liquid modification boiling at 237° . According to R. Schultz, however (*Liebig's Annalen*, clxxxvii. 274), this liquid trichlorotoluene is not a pure substance, but probably a mixture of tri- with di- and tetrachlorotoluenes, as, when treated with nitric acid, it yields a nitro-compound identical with that which is obtained from the solid modification, and on treating it with fuming sulphuric acid, the greater part of the solid modification separates out.

(0–1) *Cyanotoluene, or Benzyl Cyanide*, $C^6H^5.CH^2(CN)$. This compound, treated with zinc and hydrochloric acid, is converted into amidobenzylmethane,* $CH^2(C^6H^5)NH^2$, a base metameric with phenylethylamine or ethylaniline:



This base forms small laminæ having a characteristic odour. It volatilises with steam, dissolves sparingly in water, easily in ether, and absorbs carbonic acid from the air. Its hydrochloride forms lance-shaped crystals (Berntsen, *Ber.* viii. 691).

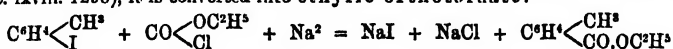
When benzyl cyanide dissolved in ammoniacal alcohol is treated with *hydrogen sulphide*, two compounds are produced, one of which crystallises in needles an inch long, which turn brown at 160° , and melt at 197° – 198° , while the other forms prisms melting at 97° , and resolved at a higher temperature into benzyl cyanide and hydrogen sulphide. This latter compound dissolves sparingly in water, freely in alcohol and ether. Its aqueous solution added to metallic salts quickly throws down metallic sulphides, and when treated with potash is resolved into potassium sulphide and benzyl cyanide. Benzyl cyanide heated with *water* at 250° is converted into α -toluamide or phenylacetamide, $C^6H^5.CH^2.CO.NH^2$, melting at 154.5° (Berntsen, *loc. cit.*) This amide is also formed by treating benzyl cyanide with ammonium acetate, according to the equation:



(Berntsen, *Ber.* ix. 429); and, according to Woddlge, by heating benzyl cyanide with an alcoholic solution of potassium hydrosulphide (p. 314).

* In Berntsen's paper this base is called phenylethylamine; but this name belongs properly to Hofmann's ethylaniline, $C^6H^5.NH(C^2H^5)$, which is an imido-base or secondary amine, whereas amidobenzylmethane is an amido-base or primary amine.

Iodotoluene, $C^6H^4I.CH^3$. The ortho-modification is very easily prepared from orthotoluidine by the action of nitrous gas and alcohol. It is liquid at ordinary temperatures, boils at 205.5° (at 211° if the entire mercury-column is in the vapour), and is oxidised by nitric acid to orthiodobenzoic acid, melting at 156° – 157° . By treatment with ethyl chlorocarbonate and sodium-amalgam (Wurtz's method, *Compt. rend.* lxxiii. 1298), it is converted into ethylic orthotoluate:



(Kekulé, *Ber.* vii. 1007).

Nitrotoluenes. (1–0) *Mononitrotoluenes, $C^6H^4(NO^2).CH^3$.*—E. J. Mills (*Phil. Mag.* [4], l. 17) prepares the para-modification by dropping toluene into red fuming nitric acid of sp. gr. 1.48, and distilling the product with water. The mixture of liquid and solid nitrotoluene which then passes over after the unaltered toluene is cooled for half an hour to -17° , and the liquid portion pipetted off. The solid *p*-nitrotoluene thus produced could not be obtained of quite constant melting point, either by sublimation, or by repeated crystallisation from alcohol, or by treatment with fuming sulphuric acid, or by partial solution in dilute alcohol. When twice crystallised from naphtha and then from alcohol, it melted at 51.31° (Mills). By oxidation with *chromic oxychloride*, it is converted into methylnitroquinone (Etard, *Compt. rend.* lxxvii. 989).

Orthonitrotoluene given to dogs exerts a poisonous action, which, however, if the dose is small, soon passes off; by repetition the animals get accustomed to it. Part of the nitro-toluene appears in the urine as orthonitrobenzoic acid (nitrohippuric acid is not formed); but the chief product of the transformation is a compound, $C^{11}H^{15}N^3O^{10} + 2\frac{1}{2}H^2O$, which crystallises in colourless silky needles; dissolves very easily in water, sparingly in cold alcohol, more readily in hot alcohol, but is insoluble in ether. It melts at 148° – 149° ; has an acid reaction; shows strong levorotatory power; reduces an alkaline cupric solution, also bismuth-solution and silver-solution; does not ferment with yeast. It is a compound of urea with *uronitrotoluenic acid*, $C^3H^3NO^3$ (Jaffé, *Russ. Zeitschr. Pharm.* 1878, 513).

(2–0) *Dinitrotoluene, $C^6H^3(NO^2)^2.CH^3$.*—The unsymmetrical modification of this compound, $CH^3 : NO^2 : NO^2 = 1 : 2 : 4$, is obtained by further nitration either of ortho- or of para-nitrotoluene, and is converted by reduction into metadiphenylenediamine (Bayer, *Ber.* vii. 1638). Mills (*Phil. Mag.* [4], l. 17), by treating toluene with a mixture of nitric and sulphuric acids, obtained a dinitrotoluene which after two crystallisations from light petroleum and from alcohol, melted at 69.23° . Liquid mononitrotoluene treated at ordinary temperatures with fuming nitric acid yielded a dinitrotoluene, which after purification melted at 69.17° , but after it had been kept for nineteen months the melting point rose to 69.6° . Solid nitrotoluene treated in small quantities with red fuming nitric acid yielded a dinitro-compound melting at 69.17° ; when larger quantities were used, the product melted at 69.57° . Dinitrotoluene treated with *sodium-amalgam* yields a black uncrystallisable mass (Miehler, *Liebig's Annalen*, clxxv. 150).

(3–0) *Trinitrotoluene, $C^6H^2(NO^2)^3.CH^3$,* is obtained by nitrating toluene with fuming nitric acid and treating the product with a mixture of nitric and fuming sulphuric acid. After recrystallisation from light petroleum and alcohol, it melted at 78.85° . It is not altered by boiling for thirty-six hours with red fuming nitric acid. Liquid nitrotoluene heated with nitric and fuming sulphuric acids yielded a trinitrotoluene which melted at 78.88° . The trinitrotoluene obtained in like manner from solid nitrotoluene did not exhibit a constant melting point till it had been submitted to a repetition of the treatment. It then melted at 80.54° .

Nitrobromotoluenes, $C^6H^3(NO^2)Br.CH^3$. Parabromotoluene yields by nitration two solid mononitro-derivatives, one melting at 45° , the other at 34° . The former yields by reduction a bromotoluidine, $C^6H^4(NH^2)Br.CH^3$, convertible by the action of sodium-amalgam and water into orthotoluidine: hence it is an ortho-para-compound, $CH^3 : NO^2 : Br = 1 : 2 : 4$.* Consequently the modification melting at 34° must be the meta-para-compound $1 : 3 : 4$, and this conclusion is confirmed by its formation from metanitroparatoluidine, $CH^3 : NO^2 : NH^2 = 1 : 3 : 4$, by converting this base into the diazoperbromide and decomposing the latter with alcohol. It crystallises from alcohol in slender yellow needles (Wroblewsky a. Kurbatow, *Zeitschr. f. Chem.* 1870, 165; Beilstein a. Kuhlberg, *Liebig's Annalen*, clviii. 335; Wroblewsky, *Ber.* viii. 573).

An *orthonitro-metabromotoluene, 1 : 2 : 3* or *1 : 2 : 5*, is formed on agitating metabromotoluene for a considerable time with moderately strong nitric acid, and separates

* Compare vii. 1167, where this nitrobromotoluene is described as the *m-p*-modification.

on addition of water as a pale yellow oil solidifying at -17° to a crystalline pulp which may be freed from adhering liquid by pressure between paper. When purified by repeated crystallisation from alcohol, it forms hard, brittle, very large, well-defined rhombic crystals, prismatic or flattened according to the strength of the solution from which they have separated. Both the crystallisation and the dissolution of the crystals in alcohol are accompanied by strong decrepitation. By reduction with tin and hydrochloric acid, this nitrobromotoluene is converted into a metabromorthotoluidine.

The liquid portion of the product is not a distinct modification, as supposed by Wroblewsky (*Zeitschr. f. Chem.* 1870, 240), but a mixture of the compound just described with unaltered metabromotoluene or a dinitrobromotoluene (E. A. Grete, *Ber.* viii. 565).

The *symmetrical* or *m-m*-modification, 1 : 3 : 5, prepared by elimination of the amido-group from nitrobromoparatoluidine, $C^6H^3H.Br.NH^2.NO^2.H$, crystallises from alcohol in shining white prisms, melts at 86° , and boils at 269° – 270° (Wroblewsky, *Ber.* viii. 573).

Nitrochlorotoluenes. Two *nitroparachlorotoluenes*, $C^6H^3(NO^2)Cl.CH^3$, one melting at 8° – 9° , the other at 34° – 35° , are obtained by direct nitration of *p*-chlorotoluene (Engelbrecht, *Ber.* vii. 797).

(1–1) *Orthonitrochlorotoluene*, or *Orthonitrobenzyl Chloride*, $C^6H^4(NO^2).CH^2Cl$ [$NO^2 : CH^2Cl = 1 : 2$], is formed by the action of chlorine on orthonitrotoluene at 150° – 200° , as a viscid oil which has an agreeably aromatic odour, exerts a burning action on sensitive parts of the skin, and solidifies after a while to a network of slender needles. With silver nitrate it forms orthonitrobenzyl acetate, $C^6H^4(NO^2).CH^2(OC^2H^3O)$ (Wachendorff, *Ber.* viii. 1101).

A nitrobenzyl chloride is also formed by dropping benzyl chloride into fuming nitric acid cooled to -15° , and may be purified by washing and recrystallisation from alcohol. By digestion with aqueous ammonia at 100° it is easily converted into secondary nitrobenzylamine, $(C^6H^4NO^2.CH^2)^2NH$, and tertiary nitrobenzylamine, $(C^6H^4NO^2.CH^2)^3N$ (p. 317).

(1–2) *Nitrochlorotoluene*, or *Nitrobenzylene Dichloride*, $C^6H^4(NO^2).CHCl_2$, is formed by the action of fuming nitric acid on benzylene dichloride cooled with water, together with large quantities of benzoic acid and benzaldehyde, which may be removed by treating the product with aqueous sodium carbonate and acid sodium sulphite. The nitrobenzylene dichloride which then remains is converted by oxidation into paranitrobenzoic acid (Hübner a. Bente, *Ber.* vi. 803. See p. 320).

Nitrotrichlorotoluene, $C^6H(NO^2)Cl^3.CH^3$, is prepared by dropping nitric acid of sp. gr. 1.52 on gently warmed pulverised trichlorotoluene till the whole is dissolved, and precipitating with water. When purified by crystallisation from alcohol or benzene it forms long white needles melting at 88.5° . 100 pts. alcohol at 20° dissolve 4.9 pts. of it. By tin and hydrochloric acid it is converted into a trichlorotoluidine which melts at 91° (R. Schultz, *Liebigs Annalen*, clxxxvii. 274).

Dinitrochlorotoluene, $C^6(NO^2)^2Cl.CH^3$, prepared by treating trichlorotoluene with a mixture of 2 pts. nitric acid (sp. gr. 1.52) and 1 pt. strong sulphuric acid, crystallises from a large quantity of hot alcohol in small yellow needles, easily soluble in benzene, melting at 225° (Schultz).

Dinitro-p-iodotoluene, $C^6H^2(NO^2)^2I.CH^3$, is formed, together with other compounds, by nitration of para-iodotoluene, and separates in colourless crystals melting at 138° (Glassner, *Ber.* viii. 561).

AMIDOTOLUENES, $C^6H^5N = C^6H^4NH^2$.

I. (1–0) Amidotoluenes, Toluidines, Tolyamines, $C^6H^4(NH^2).CH^3$.

PARATOLUIDINE. ORDINARY TOLUIDINE.—To separate this base from ortho- or pseudotoluidine, R. Bindschedler (*Ber.* vi. 1361) dissolves 2500 g. oxalic acid in 25 litres of boiling water, then slowly pours into the solution 10 kg. commercial toluidine, heats the liquid once more to the boiling point, leaves it to cool to 60° with continual stirring, and filters quickly from the crystalline precipitate which forms. This precipitate pressed, washed with water, decomposed with caustic soda, and distilled, yields crystalline paratoluidine. The cooled filtrate is mixed, with stirring, with 2 kg. oxalic acid, whereby a further crystalline precipitate is obtained, consisting of the oxalates of ortho- and para-toluidine, which is set aside for a subsequent preparation of the latter. When the filtered liquid no longer gives a precipitate on agitation with a strong solution of oxalic acid, it is distilled with soda-ley, and the

oily distillate is dried and rectified. The product thus obtained consists of technically pure *orthotoluidine*.

A similar process, founded on the sparing solubility of the acid oxalate of *p*-toluidine in ether free from alcohol, may be applied to the volumetric estimation of the two bases when mixed. On adding oxalic acid to the ethereal solution of the bases, the acid oxalate of *p*-toluidine is first formed, while the *o*-toluidine remains free till the *p*-toluidine is completely saturated. Any excess of oxalic acid that may be added is easily estimated by mixing the liquid with titrated toluidine. Any *o*-toluidine oxalate that may be formed at the same time is thus decomposed, with formation of acid oxalate of *p*-toluidine and free *o*-toluidine (Rosenstiehl, *Bull. Soc. Chim.* [2], xvii. 4). Lorenz (*Ber.* vii. 448) observes that the end of the reaction (*i.e.* the complete precipitation of the para-compound in the ethereal solution) is not easy to recognise. He therefore introduces into the ethereal solution a slip of litmus-paper, which, since oxalate of *orthotoluidine* acts upon litmus-paper, turns red on addition of any excess of oxalic acid beyond that which is required to precipitate the whole of the *p*-toluidine. Still greater exactness may be obtained by adding at once an excess of oxalic acid, filtering from the separated *p*-toluidine oxalate, washing with ether, evaporating, dissolving the residue in a small quantity of water, and titrating the excess of oxalic acid with a decinormal solution of soda. The difference between the quantity of oxalic acid thus found and the amount employed gives the quantity of oxalic acid which has combined with the *paratoluidine*.

Reactions of Paratoluidine. 1. *Oxidation*.—*Paratoluidine* treated with *potassium permanganate* is oxidised to azotoluene or ditolyldiazin, $C^{14}H^{14}N^2$; together with a red substance of the same composition, which when treated with ammonia and hydrogen sulphide is converted into symmetrical ditolyl-hydrazine or hydrazotoluene, $C^{14}H^{14}N^2$ (Barsilowsky, *Ber.* viii. 895). See also Hoogewerff a. van Dorp (*Ber.* x. 1936; xi. 1202).

2. *Reaction with Iodine Chloride*.—This compound, added to a solution of *p*-toluidine in hydrochloric acid, converts it into diiodo-*p*-toluidine (Michael a. Norton, *Ber.* xi. 107).

3. *With Mercuric Chloride*.—When an alcoholic solution of *p*-toluidine is poured upon an alcoholic solution of mercuric chloride so as to form a layer above it, the compound $HgCl^2.N(C^6H^7NH^2)Hg[NH^2(C^6H^7)Cl]^2$ is gradually formed (O. Klein, *Ber.* xi. 743).

4. *With Monochloroacetic acid*.—*Paratoluidine* (2 mol.) heated with 1 mol. chloroacetic acid yields tolyl-glycoccine, $C^6H^7.NH.CH^2.CO^2H$, and with ethyl chloroacetate the corresponding ether. *Chloroacetamide* and toluidine heated together in molecular proportion till they fuse yield tolyl-glycollamide, $C^6H^7.NH.CH^2.CONH^2$, and in like manner tolyl-glycollanilide and tolyl-glycolltoluide may be produced (P. F. Meyer, *Ber.* viii. 1158). See GLYCOLLAMIDES (p. 882). When a solution of toluidine in absolute alcohol is heated with *chloroacetic* and *thiocyanic acids*, a brisk reaction takes place, and crystals separate, which when purified by recrystallisation from alcohol and boiling with ether, have the composition $C^{10}H^{12}N^2SO^2$, and melt at 176° – 182° . Their formation is represented by the equation:



(Nencki, *J. pr. Chem.* [2], xvi. 1).

5. *With Chloral*.—Toluidine dissolves with rise of temperature in chloral, producing trichlorethylidene-ditolyldiamine, $CCl^3.CH[NH(C^6H^4.CH^3)]^2$ (Wallach, vii. 1179).

6. *With Ethylene Oxide*.—The two substances, heated together in molecular proportion at 100° in a closed flask, unite and form oxethylenetoluidine, $C^6H^{13}NO$ (Demole, *Ber.* vii. 635).

7. *With Dinitrochlorobenzene*, toluidine forms chloronitrophenyl-*p*-tolylamine, $C^6H^4Cl(NO^2).NH(C^6H^4.CH^3)$.

8. *Paratoluidine* unites with *picramide*, forming the compound $C^6H^7N.C^6(NO^2)^2H^2.NH^2$, which crystallises in shining black needles having a greenish reflex (Mertens, *Ber.* xi. 843).

9. *Paratoluidine* unites with *paraphenolsulphonic acid*, producing great rise of temperature, and the solid mass which forms on cooling, yields when crystallised from hot water, large semi-transparent, colourless, or yellowish prisms, which cleave readily and melt at 202° . 100 pts. water at 17° dissolve 5.18 pts. of the compound (Lecco, *Monit. scientif.* [5], iv. 423).

ORTHOTOLUIDINE or PSEUDOTOLUIDINE, $C^6.CH^3.NH^2.H^4$.—On the separation of this base from the *para*-modification, see p. 1995.

Reactions.—1. By the action of *iodine chloride*, it is converted into monoiodo-*orthotoluidine* (Michael a. Norton). 2. By oxidation with *potassium permanganate*, it yields *o*-tolyl-diazin (Hoogewerff a. van Dorp, *Ber.* xi. 1202).

3. With *potassium ferricyanide*, it yields uncrystallisable products of oxidation (Barsilowsky, *Ber.* xi. 2156). 4. Heated at 200° – 220° with *methyl alcohol* and hydrochloric acid, it is converted into dimethyl-*o*-toluidine boiling at 206° – 207° . With *picramide*, it forms a compound similar to the *p*-toluidine compound (p. 1996). 5. It unites with *mercuric chloride*, forming a compound which melts at 113° – 115° (Klein, *Ber.* xi. 743). 6. A mixture of *o*-toluidine hydrochloride and a strong solution of zinc chloride cooled to a low temperature (-5°) deposits colourless, concentrically grouped, tabular, anhydrous crystals, consisting of the double salt $\text{ZnCl}_2 \cdot 2(\text{C}_6\text{H}_7\text{N}, \text{HCl})$ (Bibanow, *Monit. scientif.* [3], iv. 925).

The salts of orthotoluidine yield by oxidation a basic substance, $\text{C}_6\text{H}_7\text{N}$ (also occurring in crude aniline-black), having a blue-violet colour, slightly soluble in alcohol, easily in chloroform and aniline, and forming green salts. Hydrochloric acid, added to the chloroform solution, throws down the green hydrochloride (Nietzki, *Ber.* xi. 1093).

METATOLUIDINE, $\text{C}_6\text{H}_3\text{H}_3\text{N} \cdot \text{H}_2$.—F. Lorenz (*Ber.* vii. 448) prepares this base by the following process. Paratoluidine is converted by means of glacial acetic acid or acetic anhydride into paracetoluide; this into its metanitro-derivative, by adding it in small portions to nitric acid of sp. gr. 1.475, and precipitating with snow; and the nitroacetoluide by gentle heating with alcoholic potash into metanitroparatoluidine, $\text{C}_6\text{H}_3\text{H}_3\text{N} \cdot \text{H} \cdot \text{NO}_2 \cdot \text{NH}_2 \cdot \text{H}_2$ (p. 1999). This nitro-base is then mixed to a thin paste with nitric acid; nitrous gas is passed into the mixture; the clear light-brown solution is mixed in a well-cooled vessel with the calculated quantity of dilute sulphuric acid; and the resulting precipitate is washed with ether-alcohol. The diazin-compound thus obtained is converted by boiling with absolute alcohol into metanitrotoluene, which may be purified by distillation with steam, and when reduced by tin and hydrochloric acid yields metatoluidine.

Metatoluidine is a colourless oil, which becomes coloured and resinises on exposure to the air. It has a density of 0.998 at 25° , and boils at 197° . The free base does not change the colour of litmus, but its salts have an acid reaction, so that they might be analysed by titration with soda-ley. They quickly acquire a rose tint.

The *hydrochloride* crystallises from water in rosettes of thin laminae; from alcohol in thin pale-red scales; it is very soluble in alcohol and in water; the aqueous solutions are easily supersaturated. The *nitrate* separates by slow crystallisation in large, thick, rhombic tablets, having a pale-red colour, slightly soluble in ether, very soluble in alcohol, less easily in water, with which it readily forms supersaturated solutions. The *sulphate* forms radiate groups of long, brittle, faintly reddish, transparent needles, easily soluble in water, sparingly in alcohol, insoluble in ether.

Oxalates.—The *acid oxalate*, $\text{C}_6\text{H}_3\text{N} \cdot \text{C}_2\text{H}_2\text{O}_4$, forms large nodular groups of slender needles having a silky lustre, sparingly soluble in water, alcohol, and ether. They begin to volatilise at 75° (possibly from loss of base). The *sesquibasic oxalate*, $(\text{C}_6\text{H}_3\text{N})_2(\text{C}_2\text{H}_2\text{O}_4)_3$, is formed on heating the aqueous solution of the acid salt with the free base, and separates from the warm solution in step-like groups of hard rhombic laminae: it is also formed, in the preparation of the acid salt, when the quantity of oxalic acid present is not sufficient for the formation of the latter. It is not decomposed by recrystallisation. The *normal oxalate* is formed on mixing the warm alcoholic solutions of oxalic acid and metatoluidine, the latter being in large excess, and separates in soft rhombic laminae which contain 1 mol. water, and when dried in the air have very much the aspect of cholesterin; it is very unstable (Lorenz).

The following table (drawn up by Lorenz) contains a comparison of the reactions of the three toluidines with the reagents which, according to Rosenstiehl, are characteristic for ortho- and para-toluidine.

1. The base dissolved in $\text{SH}^2\text{O}^4 \cdot \text{H}^2\text{O}$ is treated with a solution of *chromic acid* in sulphuric acid of the same concentration. The mixture is coloured:

Orthotoluidine	Metatoluidine	Paratoluidine
Blue, changing on dilution to a permanent red-violet.	Yellow-brown, which becomes greenish-yellow on addition of a small quantity of water, and on further dilution colourless.	Yellow.

2. *Nitric acid* is added to a solution of the base in $\text{SH}^2\text{O}^4 \cdot \text{H}^2\text{O}$.

An orange-colour is produced, and with very concentrated solutions a brown, becoming yellow on dilution.

The mixture becomes at once red, changing quickly to intense blood-red, then to a dirty dark red, and on dilution to orange.

Blue streaks are produced, which soon tinge the whole liquid; after a minute the colour becomes violet, then red, and after some hours brown.

3. To a solution of the base in equal volumes of water and ether, a few drops of a clear solution of *bleaching powder* are added.

The layer of water becomes first yellow and then brown. The ether separated from the water, and when treated with dilute sulphuric acid is permanently coloured a red violet.

The layer of water becomes a thick brownish-yellow: the ether assumes a reddish colour. When separated and shaken with a few drops of dilute sulphuric acid, the under surface of the ether is coloured violet.

No reaction.

Bromotoluidines. E. A. Grete (*Ber.* vii. 796), by treating metabromotoluene with nitric acid, obtains a mixture of nitro-products which by reduction yields a metabromotoluidine liquid at ordinary temperatures and volatilising with steam. Its sulphate crystallises in laminae or six-sided prisms; the nitrate in six-sided prisms or plates; the oxalate in needles; the hydrochloride in very soluble needles, branched like those of sal-ammoniac.

Metabromorthotoluidine, $C^6H^3BrNH^2$, which Wroblewsky obtained by brominating orthotoluidine and decomposing the resulting ortho-acetoluide with potash (vii. 1176), is also produced by the action of tin and hydrochloric acid on the corresponding nitrometabromotoluene (*fi.* p. 54°–55°). It crystallises from alcohol in well-defined rhombohedrons having their upper and lower summits alternately truncated. It volatilises with steam, melts at 57.5°–58°, dissolves very easily in alcohol, and with moderate facility in water. By sodium-amalgam it is completely decomposed, apparently with formation of toluene and ammonia. By boiling with glacial acetic acid it is converted into *metabromacetoluide*, melting at 156°. The *sulphate*, $(C^6H^3BrN)^2H^2SO^4$, crystallises from its aqueous solution by slow evaporation in regular quadratic tablets. The *nitrate*, $C^6H^3BrN.HNO^3$, forms six-sided, often flattened needles with pyramidal summits. The *hydrochloride*, $C^6H^3BrN.HCl$, forms long, thin, often flattened needles very soluble in water. The *oxalate*, $(C^6H^3BrN)^2.C^2H^2O^4$, crystallises in tufts of long needles (Grete, *Ber.* viii. 565).

Hübner a. Roos (*Ber.* vi. 799) have obtained, by nitration of parabromotoluene, a mixture of nitrobromotoluenes, yielding by reduction:

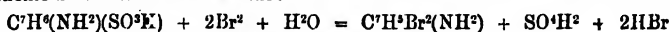
(1). *α-Parabromotoluidine*, melting at 32° [apparently identical with the bromotoluidine described by Hübner a. Wallach as melting at 31°, by Beilstein at 30°, by Kürner, at 27°, and by Wroblewsky (vi. 1104) at –2°]. The *hydrochloride* of this bromotoluidine forms large, six-sided, rhombic tablets; the *nitrate* transparent, pale-red, rhombic tablets, soluble in 120.9 pts. water at 11.5°; the *sulphate*, $2C^6H^3BrN.H^2SO^4$, colourless, sparingly soluble laminae.

(2). *β-Parabromotoluidine*, melting at 75°, or, according to Wroblewsky, at 67°.

(3). An *orthobromotoluidine*, in the form of a liquid which does not solidify at 0°, and forms crystalline salts, the hydrochloride and nitrate crystallising in rhombic tablets, the sulphate in needles.

On *Symmetrical Bromotoluidine*, $CH^3 : NH^2 : Br = 1 : 3 : 5$, melting at 34.5°–37°, see p. 1988.

Dibromotoluidines, $C^6H^3Br^2(NH^2).CH^3$. — On the modification $C^6H^3 : Br : NH^2 : Br = 1 : 2 : 3 : 6$ and $1 : 2 : 4 : 5$, see p. 1990. A dibromotoluidine is formed, together with sulphuric acid, on heating paramidotoluenemeta-sulphonic acid with 2 mol. bromine:



(*IR.* v. Pechmann, *Liebig's Annalen*, clxxii. 195; *Ber.* vii. 718).

Tribromotoluidine, $C^6H^3Br^3.CH^3$. — This compound appears to be known in three modifications, the constitution of which has not however been made out. One of these, which crystallises in needles melting at 112°–113°, is formed by the action of bromine on *o*-toluidine-*m*-sulphonic acid, and on *p*-toluidine-*m*-sulphonic acid. It sublimes easily without decomposition, and does not unite with acids (pp. 2016, 2019). Another modification is obtained, together with sulphuric acid, by the action of water and bromine on amidorthobromotoluenemeta-sulphonic acid (p. 2019). It crystallises from alcohol in yellow needles and volatilises with steam in nearly white flocks which melt at 82° (Schäfer, *Ber.* vii. 1355). A third modification is obtained by adding bromine-water in excess to a cold saturated solution of metatoluidineorthosulphonic acid, as a flocculent precipitate, which when recrystallised from alcohol, with addition of animal charcoal, forms thin, fragile, faintly reddish needles melting at 95°. By cautious sublimation it may be obtained in snow-white needles melting at 101°. It is insoluble

in soda-ley and hydrochloric acid; but dissolves in strong sulphuric acid, and is precipitated therefrom by water without alteration (Lorenz, *Ber.* vii, 448).

Iodotoluidines (Michael a. Norton, *Ber.* xi. 107).

Monoiodo-toluidine, $C^6H^4(NH^2)CH^3$.—Acetorthotoluide, $C^6H^4(NH.C^2H^3O)CH^3$, dissolved in glacial acetic acid, is converted by the action of iodine chloride into iodoaceto-toluide, which crystallises from water or alcohol in short thick needles melting at 165.5° , sparingly soluble in cold, more readily in hot water, very easily in alcohol and ethyl acetate, soluble also in strong nitric acid without separation of iodine.

This iodoaceto-toluide is converted by boiling with hydrochloric acid into iodo-toluidine hydrochloride which crystallises in needles. The free base crystallises from alcohol in long white needles melting at 86° , very sparingly soluble even in hot water, easily soluble in alcohol, ether, and acetic acid; it volatilises readily with vapour of water. Heated with strong sulphuric acid it decomposes, evolving vapours of iodine. The *nitrate* crystallises in colourless needles, somewhat sparingly soluble in water. The platinochloride does not crystallise well.

The base treated with nitrous acid is converted into a diazin-compound which forms a light-yellow crystalline precipitate easily soluble in alcohol, and convertible by boiling with alcohol into the corresponding iodotoluene, which when oxidised by nitric acid yields *meta*-iodobenzoic acid melting at 184° . The base is therefore a metaiodo-orthotoluidine.

Orthotoluidine treated with iodine chloride likewise yields a monoiodorthotoluidine.

Di-iodo-p-toluidine, $C^6H^2I^2(NH^2).CH^3$, formed by the action of iodine chloride on paratoluidine dissolved in hydrochloric acid, crystallises in ramified groups of slender needles, melting at 124.5° , moderately soluble in cold, freely in hot alcohol.

Nitrotoluidines.

Metanitroparatoluidine, $C^6CH^3.H.NO^2.NH^2.H^2$. Lorenz (*Liebig's Annalen*, clixii. 177) prepares this compound by converting paracetoluide into its metanitro-derivative (m. p. 92°), and treating the latter at a gentle heat with alcoholic potash. It crystallises from alcohol in thick red prisms, melting at 109° ; after recrystallisation from water at 114° . According to Panebianco (*Gazz. chim. ital.* 1879, 358), the crystals are monoclinic, having the axial ratio $a : b : c = 1.35781 : 1 : 1.75472$. Angle $ac = 54^\circ 51'$. According to Friederici (*Ber.* xi. 1970), this nitrotoluidine crystallises from dilute alcoholic solution in brick-red shining laminae, from concentrated alcoholic solution in slender needles or long thick prisms, and volatilises with water-vapour in red flocks made up of needle-shaped crystals. Moderately strong hydrochloric acid dissolves it readily when heated, and the solution on cooling deposits the *hydrochloride*, $C^6H^3(NO^2)N.HCl$, in well-defined light-yellow prisms, which are instantly decomposed by water. The *nitrate*, $C^6H^3(NO^2)N.HNO^2$, forms light yellow, highly lustrous, six-sided plates or slender needles likewise decomposed by water.

Methyl-toluidines.

Mono- and Di-methyl-p-toluidine are formed when vapour of methyl chloride is passed into *p*-toluidine boiling in a reflux apparatus through which a current of steam is passed, 3.5 pts. of the toluidine attacked being converted into the mono-methyl-derivative to 1 pt. converted into the dimethyl-derivative. The ethereal extract of the crude product freed from unattacked toluidine by sulphuric acid, leaves on evaporation an oil which becomes very hot in contact with acetic anhydride, and after repeated distillation yields *acetomonomethylparatoluidine*, $C^6H^2.N(CH^3)(C^2H^3O)$, which forms colourless crystals, melts at 83° , boils at 283° , dissolves easily in alcohol and ether, sparingly in water. By successive saponification with hydrochloric acid and soda-ley, it yields *monomethylparatoluidine* as a colourless aromatic oil boiling at 208° . *Nitroso-methyl-p-toluidine*, $(C^6H^3)N(CH^3)(NO)$, obtained by the action of potassium nitrite on methyl toluidine dissolved in hydrochloric acid, is insoluble in water, easily soluble in alcohol and ether, and melts at 54° .

Dinitromethylparatoluidine, $C^6H^2.NH[CH(NO^2)^2]$, produced by the action of fuming nitric acid on a solution of the acetyl-compound in glacial acetic acid, crystallises from dilute alcohol in light-red needles melting at 129° , and dissolving, without decomposition, in glacial acetic and hot hydrochloric acid (A. L. Thomsen, *Ber.* x. 1582).

Dimethyl-p-toluidine, $C^6H^3N = (C^6H^2)(CH^3)^2N = C^6H^4[N(CH^3)^2].CH^3$.—On the formation of this base by intramolecular interchange from trimethyl-phenylammonium iodide, and its subsequent conversion into methyl-xylidine and eumidine, see A. W. Hofmann (vii. 57). It is also formed by distillation of trimethyl-*p*-tolylammonium hydroxide, passing over as a colourless aromatic oil which boils at 208° .

Dimethyl-orthotoluidine, prepared in like manner, boils at 183°. *Trimethyl-orthotolyl-ammonium Iodide* crystallises in large needles which acquire a purple colour on exposure to the air (A. L. Thomsen, *loc. cit.*)

Bromodimethyl-metatoluidine is formed by the action of bromine on dimethyl-metatoluidine dissolved in two or three times its volume of hydrochloric acid. The light yellow liquid thereby produced is poured off from an oil which separates, into cooled soda-ley, and the crystals which form are freed by pressure from adhering liquid, and recrystallised from alcohol. The compound is thus obtained in white shining laminae, unctuous to the touch, insoluble in water, easily soluble in the other ordinary solvents; it melts at 98°, and boils at 276° (Wurster a. Riedel, *Ber.* xii. 1796).

Nitroso- and Nitro-derivatives of Dimethyl-m-toluidine (Wurster a. Riedel, *loc. cit.*).—*Nitroso-dimethyl-m-toluidine Hydrochloride*, $C^6H^{12}(NO)N.HCl$, is deposited on adding a saturated solution of sodium nitrite to a solution of dimethyl-metatoluidine in dilute hydrochloric acid. It is sparingly soluble in cold, but dissolves in hot water in presence of hydrochloric acid, and crystallises on cooling in yellow needles. The free base obtained by decomposing the hydrochloride with sodium carbonate crystallises from ether in green plates or needles melting at 92°; from a chloroform solution mixed with ligroin in moss-green needles; from benzene in dark-green efflorescent crystals containing benzene; from water in laminae. It forms steel-blue double salts with amines (aniline, toluidine), is converted by potash-ley into a red-brown azoxy-compound, and is resolved by soda-ley into dimethylamine and a nitrosocresol, $C^6H^4(NO)(OH).CH^3$, which crystallises in white needles, melting at 145°–150°, soluble in alcohol, benzene, chloroform, and glacial acetic acid, slightly soluble in boiling water and in ether; yielding an acetyl-derivative which forms prismatic crystals soluble in alcohol and melting at 92°; and converted by the action of nitric acid on its solution in glacial acetic acid into trinitrocresol.

Nitrosodimethyl-m-toluidine, treated with tin and hydrochloric acid, is converted into a dimethyl-tolylene-diamine, $N^2H^2(CH^3)^2(C^6H^4)$, which, when oxidised by sulphuric acid and manganese dioxide, yields a crystalline compound (m. p. 67°) identical with the toluquinone $C^6H^4O^2$ (*q.v.*) prepared from paratoluidine. Dimethyl-tolylene-diamine is therefore a derivative of paratoluidine, and since it is obtained by reduction of nitrosodimethyl-m-toluidine, it follows that the nitroso-group in the latter compound must occupy the para-position with regard to the amido-group. Hence the constitution of nitrosodimethyl-m-toluidine must be represented by the

formula $C^6H^4.NO.H.H.N(CH^3)^2.H$ (Riedel, *Ber.* xiii. 126).

Nitrodimethylmetatoluidine is formed when potassium permanganate is added to an aqueous solution of nitrosodimethylmetatoluidine hydrochloride, and may be extracted from the liquid with ether. It crystallises in long yellow needles melting at 84°. The corresponding *dinitro*-derivative is obtained in yellow needle-shaped crystals melting at 107°, by adding nitric acid to a solution of dimethylmetatoluidine in glacial acetic acid. If the nitration is carried on with dilute nitric acid, or if the mixture of sulphuric and nitric acids is kept perfectly cold, three nitro-derivatives are obtained, viz., the mono-nitro-derivative melting at 84°, and two dinitro-derivatives melting at 107° and 168° respectively. The latter is less soluble in alcohol than the dinitro-compound which melts at 107° (Wurster a. Riedel).

On *Colouring Matters* derived from Methyl- and Dimethyl-toluidine, see Monnet, Reverdin a. Nölting (*Ber.* xi. 2278; *Chem. Soc. J.* xxxvi. 310).

(0-1) **Amidotoluene, or Benzylamine**, $C^6H^5.CH^2(NH^2)$. This base, originally obtained by the action of ammonia on benzyl chloride (v. 867), and afterwards by decomposing benzyl isocyanate or isocyanurate with potash (vii. 181), may also be prepared by the action of alcoholic potash on benzyl-acetamide (from acetamide and benzyl chloride). The *hydrochloride* separates from alcoholic solution in large plates. The *platinochloride* crystallises in orange-coloured plates, the *sulphate* in transparent crystals freely soluble in water (C. Rudolph, *Ber.* xii. 1297).

Tri-p-bromobenzylamine, $(C^6H^4Br)^3N = (CH^2Br.C^6H^4)^3N$, is formed by the action of alcoholic ammonia at ordinary temperatures on parabromobenzyl bromide, and separates immediately as a crystalline pulp, together with a substance scarcely soluble in alcohol. The triamine is insoluble in water, but dissolves in alcohol, ether, benzene, and carbon sulphide, and crystallises from alcohol in prisms melting at 78°–79°.

The substance nearly insoluble in alcohol is the corresponding *hydrobromide*, $(C^6H^4Br)^3N.HBr$. It crystallises in white scales melting at 270°, insoluble in water, easily soluble in ether (Jackson a. Lowery, *Ber.* x. 1209).

Mono-, Di-, and Tri-orthobromobenzylamines are formed by heating

α -bromobenzyl bromide at 100° for two hours with alcoholic ammonia. The tertiary base, $(C^6H^4Br.CH^2)^2N$, separates from the product in crystals, which, after recrystallisation from ether, melt at 121.5° ; its *platinochloride*, $[(C^6H^4Br.CH^2)^2NH]^2PtCl^6$, is insoluble in water and in ether, and very sparingly soluble in alcohol. The primary base, $C^6H^4Br.CH^2NH^2$, is obtained from the liquid filtered from the crystals of the tertiary base by evaporating to dryness, treating the residue with carbonic acid, exhausting with water (the secondary base then remaining undissolved), mixing the extract with caustic soda, and washing the oil thereby precipitated. It is a colourless oil yielding a *carbonate* in white crystals melting at 95° , and a *hydrochloride*, in needles melting at 208° , both soluble in water and in alcohol. The *platinochloride*, $(C^6H^4Br.CH^2NH^2)^2PtCl^6$, forms orange-yellow needles insoluble in ether, slightly soluble in water and in alcohol. The secondary base, $(C^6H^4Br.CH^2)^2NH$, solidifies in a freezing mixture to rhombic needles melting at 36° , having a pleasant odour, insoluble in water. The *hydrochloride* melts at 166° ; the *platinochloride*, $[(C^6H^4Br.CH^2)^2NH]^2PtCl^6$, is a dark yellow precipitate insoluble in ether, moderately soluble in alcohol and in water.

Chlorobenzylamines.—*p*-Monochlorobenzylamine, $C^6H^4Cl.NH^2$, is liquid. Di-*p*-chlorobenzylamine, $(C^6H^4Cl)^2NH$, melts at 89° ; tri-*p*-chlorobenzylamine, $(C^6H^4Cl)^3N$, at 196° (Jackson a. Field, *Ber.* xi. 904).

Iodobenzylamines.—Di- and Tri-*p*-iodobenzylamine, $(C^6H^4I.CH^2)^2NH$, and $(C^6H^4I.CH^2)^3N$, are produced simultaneously by boiling *p*-iodobenzyl bromide (p. 2007) with alcoholic ammonia. The tri-derivative, which is the less soluble part of the product, may be purified by recrystallisation from ether. It forms white needles, melting at 114° – 115° , insoluble in water and in cold alcohol, slightly soluble in hot alcohol, also in ether, benzene, and carbon sulphide. The *platinochloride*, $[(C^6H^4I.CH^2)^2NH]^2PtCl^6$, crystallises in yellow needles nearly insoluble in water and in alcohol. Di-*p*-iodobenzylamine forms white needles having an aromatic odour and melting at 76° . It is insoluble in water, but dissolves readily in hot alcohol, ether, benzene, and carbon sulphide. The *platinochloride*, $[(C^6H^4I.CH^2)^2NH]^2PtCl^6$, forms light yellow crystals nearly insoluble in water and in alcohol (Mabery a. Jackson, *Ber.* xi. 55).

Ethylbenzylamines. Diethylbenzylamine, $NH(C^2H^5)^2$, formed by heating diethylamine with benzyl chloride in molecular proportions, boils at 211° – 212° (V. Meyer, *Ber.* x. 309).

Triethylbenzylammonium Iodide, $N(C^2H^5)^3(C^6H^5)I$.—According to Ladenburg a. Struver (*Ber.* x. 43), and Ladenburg (*ibid.* 561, 1152, 1634), on the one hand, and V. Meyer (*ibid.* 309, 964, 978, 1291) on the other, this compound admits of two modifications, $N(C^2H^5)^3C^6H^5I$ and $N(C^2H^5)^2C^6H^5.C^2H^5I$, the former, designated as above, being obtained by the union of triethylamine and benzyl iodide, the latter, called benzyl-triethylammonium iodide, from benzyl-diethylamine and ethyl iodide by heating with water; also, together with the hydriodides of benzyldiethylamine and benzyloethylamine, by heating benzylamine at 130° with ethyl iodide. Both these iodides crystallise in large white crystals; both yield the same periodide, $N(C^2H^5)^3C^6H^5I^3$, which is formed either by direct combination or by boiling the solutions of the monoiodides with hydriodic acid, and crystallises in metallicallly lustrous prisms melting at 87° ; moreover, the corresponding picrates resemble each other very closely, consisting of yellow prisms melting below 100° . The *platinochlorides*, however, are, according to Ladenburg a. Struve, not identical, that of triethylbenzylammonium chloride crystallising in tufts of prisms, or in well-defined, apparently monoclinic crystals, whereas that of benzyltriethylammonium chloride forms tubular crystals, apparently rhombic, which, by keeping or recrystallisation, are converted into the former *platinochloride*. According to Ladenburg, also, the iodide of triethylbenzylammonium changes into that of benzyltriethylammonium when its solutions are concentrated. Altogether, however, the difference between the two iodides does not appear to be satisfactorily made out.

Phenylbenzylamine, or *Benzylaniline*, $NH(C^6H^5)(CH^2.C^6H^5)$. This base, metamerie with Hofmann's tolylaniline (iv. 454), is formed: (1). Together with aniline hydrochloride, by heating benzyl chloride (b. p. 176°) with aniline at 160° for twenty-four hours:



(M. Fleischer, *Liebig's Annalen*, cxxxviii. 225).

(2). By the action of nascent hydrogen (zinc-dust and HCl, or sodium-amalgam and water) on benzoethianilide (p. 1924):



(Bernthsen a. Trompeter, *Ber.* xi. 1756).

Benzylaniline solidifies at low temperatures to a crystalline mass, and crystallises from hot alcohol in four-sided prisms, insoluble in water, easily soluble in alcohol and ether. It melts at 32° , remains liquid at 12° , and boils at 310° (Fleischer); melts at 33° (B. and T.) [Tolylaniline, $\text{NH}(\text{C}^6\text{H}_5)(\text{C}^6\text{H}_4\text{CH}_3)$, melts at 87° and boils at 334.5° (corr.)] The *hydrochloride*, $\text{C}^{11}\text{H}^{11}\text{N}.\text{HCl}$, forms white well-defined crystals easily soluble in water and alcohol, sparingly in ether, and turning green on exposure to the air or on drying (Fleischer); white laminae melting at 197° (B. and T.) The *platinichloride* forms concentric groups of yellow-red laminae (B. and T.) The *cadmichloride*, $\text{C}^{11}\text{H}^{11}\text{N}.\text{CdCl}_2$, dissolves readily in hot alcohol, and crystallises in tufts of white needles which are decomposed by drying or by the action of water (Fleischer).

In contact with *mercuric chloride*, benzylaniline forms a green mass which dissolves with blue colour in alcohol, assumes a darker colour on prolonged heating, and then dissolves in alcohol with crimson colour. Benzylaniline heated with *benzoyl chloride* forms a yellowish oil, which gradually solidifies in contact with water and alkali, and crystallises from alcohol in well-defined six-sided monoclinic prisms, consisting of phenylbenzylbenzamide, $\text{N}(\text{C}^6\text{H}_5)(\text{C}^6\text{H}_7)(\text{C}^6\text{H}_5\text{O})$. This compound is insoluble in ether, melts at 104° , and dissolves in strong nitric acid, forming a yellow nitro-compound (Fleischer).

Benzylidiphenylamine, $\text{N}(\text{C}^6\text{H}_7)(\text{C}^6\text{H}_5)^2$, formed by the action of nascent hydrogen on benzodiphenylthiamide, crystallises in long white needles melting at 86.5° – 87° . It is nearly insoluble in water, slightly soluble in cold alcohol, easily in hot alcohol and in ether; does not exhibit basic properties (Bernthsen and Trompeter).

Derivatives of Toluidine containing Acid Radicles.

Acetoluides, $\text{C}^6\text{H}_4(\text{NH}.\text{C}^2\text{H}_3\text{O}).\text{CH}_3$. *Para*-acetoluide is dimorphous. By spontaneous evaporation of its alcoholic solution it is obtained in monoclinic crystals having the axial ratio $a : b : c = 1.21654 : 1 : 0.78885$, and the axial angle $106^{\circ} 7' 20''$. Observed forms $\infty \text{P} \infty$, 0P , ∞P , $-\text{P}$, P , ∞ , $2\text{P} \infty$. Cleavage perfect parallel to 0P , less distinct parallel to $\infty \text{P} \infty$. Twin-plane parallel to 0P . In a cleavage plate parallel to 0P , the angle of the optic axes in oil was for red light $106^{\circ} 10' (\rho < \nu)$. Dispersion very weak. On cooling from a warm alcoholic solution, on the other hand, or from a supersaturated solution, the compound is deposited in orthorhombic crystals, partly transparent needles without distinct summits, partly flat needles with distinct summits, and in the latter case mostly turbid. Axes $a : b : c = 0.65147 : 1 : 0.32885$. Observed forms $\infty \text{P} \infty$, $\infty \text{P} \infty$, 0P , ∞P , $\text{P} \infty$, $2\text{P} 2$. The transparent needles exhibit only the faces $\infty \text{P} \infty$, $\infty \text{P} \infty$ and ∞P . Cleavage not recognisable. The plane of the optic axes is $\infty \text{P} \infty$; the acute bisectrix is normal to $\infty \text{P} \infty$. $\rho < \nu$. Angle $2\text{H}_a = 84^{\circ}$ for red. This case of dimorphism is the third which has been observed in the paraseries (Parebianco, *Gazz. chim. ital.* 1878, 426).

By oxidation with potassium permanganate in hot aqueous solution, *p*-acetoluide yields an acetamidobenzoic acid, $\text{C}^6\text{H}_4(\text{NH}.\text{C}^2\text{H}_3\text{O})(\text{CO}_2\text{H})$, which melts with partial decomposition at about 250° , and is converted by hydrochloric acid into the hydrochloride of paramidobenzoic acid (A. W. Hofmann, *Ber.* ix. 1299).

On the reaction of *p*-acetoluide with *phosphorus pentachloride*, see *Ethenyl-tolylamines* (p. 746).

o-Acetoluide dissolved in glacial acetic acid is converted by iodine chloride into mono-iod-*o*-acetoluide; *p*-Acetoluide, on the other hand, is not attacked by iodine chloride (see IOTOLUIDINES, p. 1999).

Metabromorthacetoluide, $\text{C}^6\text{H}_3\text{NH}(\text{C}^2\text{H}_3\text{O}).\text{Br}.\text{H}^+$, formed by boiling metabromorthotoluidine (p. 1998) with glacial acetic acid for six hours, separates from aqueous solution in white capillary coral-like forms, which under the microscope appear to be made up of slender needles; it melts at 156° (Grete, *Ber.* viii. 565).

Benzotoluides, or Tolybenzamides, $\text{C}^{14}\text{H}^{11}\text{NO} = \text{CH}^3.\text{C}^6\text{H}_4.\text{N}.\text{Fi}.\text{CO}.\text{C}^6\text{H}_5$. The *para*-modification, obtained by treating *p*-toluidine with benzoyl chloride (v. 872), melts, according to Kelbe (*Ber.* viii. 875), at 155° , and is easily resolved by boiling with alkalis into toluidine and benzoic acid. By nitration it yields a mono- and a dinitro-compound, which may be separated by crystallisation from an alcoholic alkaline solution, the mononitro-compound crystallising out first. This latter compound forms yellow needles melting at 143° . It is insoluble in water, and is resolved by hydrochloric acid at 200° into benzoic acid and *metanitrotoluidine*, which crystallises from alcohol in red needles melting at 110° . By the action of hydrogen it is converted into *anhydroadimidobenzotoluide*, a volatile, very stable basic compound which crystallises in colourless needles, melts at 232° – 233° , is insoluble in water, but dissolves in alcohol and in aqueous potash. Its *hydrochloride* is easily decomposable, and only

sparingly soluble in cold water. The *sulphate* crystallises in red needles (Kelbe). C. A. Bell (*Ber.* vii. 1504) describes a nitrobenzotoluide obtained by the action of benzoyl chloride on nitrotoluidine (m. p. 77·5°). It crystallises in light yellow prisms melting at 172°, and is reduced by tin and hydrochloric acid to a benzoyltolylene-diamine which crystallises in colourless needles melting at 142°.

Dinitrobenzotoluidine forms colourless needles, easily soluble in alcohol and glacial acetic acid, melting at 186°. By heating with hydrochloric acid or with alcoholic potash at 150°, it is converted into a dinitrotoluidine, which dissolves in hot water, melts at 186°, and is converted by hydrogen into a base, $C^6H^4(NH^2)^2NH_2OC^6H^5$, which crystallises in grey opaque needles, soluble in alcohol and ether, and melting at 182°–183°. Its sulphate contains 1 mol. water of crystallisation. Dinitrobenzotoluide is converted by hydrogen sulphide into an amidonitrobenzotoluide, which crystallises in red needles melting at 137°–139° (Kelbe, *loc. cit.*)

Benzothiotoluide, $C^6H^5CS.NH(C^6H^5)$. See THIAMIDES (p. 1953).

Diamidotoluenes, or Tolylenediamines, $C^6H^4(NH^2)^2 = C^6H^3(NH^2)^2.CH^3$ (v. 872; vii. 1180).

PARA-ORTHOTOLYLENEDIAMINE, $CH^3 : NH^2 : NH^2 = 1 : 2 : 4$ (m. p. 99°), also called *Metatolylenediamine*. This modification is converted by boiling with excess of glacial acetic acid into a *diacetotolylenediamine* melting at 224°, which, when treated with cold fuming nitric acid, yields *nitrodiacetotolylenediamine* melting at 253°, soluble in 300 pts. of boiling acetone, insoluble in alcohol and ether. This nitro-aceto-compound dissolves with decomposition in hot hydrochloric acid, and the solution on cooling deposits red crystals which, as well as the solution, are decomposed by ammonia, yielding a *nitrotolylenediamine*, which dissolves in hot water, and crystallises in yellow-red needles melting at 154°; dissolves also in hot dilute acids, forming easily decomposable crystallisable salts, and in hot alcohol. This nitrotolylenediamine, treated with nitrogen dioxide or nitrous gas, yields a red, very stable amorphous body having the composition $C^6H^3(NO^2)(NH^2)N^2, C^6H^3(NO^2)(NH^2)(NH)$. If the reaction takes place in an acid solution, there is also formed a colourless bye-product—probably a nitroethyleresol, which gives off nitrogen when boiled with alcohol. It crystallises in shining prisms; is insoluble in water, but dissolves easily in alcohol; volatilises with steam; melts at 72°–73°, and boils at about 285° (Ladenburg, *Ber.* viii. 1209).

When *p-o*-tolylenediamine dissolved in alcohol is treated with *carbon bisulphide*, large quantities of hydrogen sulphide are given off, and on leaving the solution to digest for two days at the ordinary temperature, then evaporating it to a syrup, and exhausting with benzene, a yellow residue is left, soluble in alcohol, and on adding water to the alcoholic solution, a yellow crystalline precipitate is obtained, consisting of tolylene thiocarbamide, $N^2(C^6H^4)(CS)H^2$ (R. Lussy, *Ber.* viii. 291).

(*p-o*)-Tolylenediamine, treated with ethylechlorocarbonate, yields tolylene-urethane, $C^6H^4NH^2NH^2CO^2$, which crystallises from alcohol in dazzling white silky needles melting at 137°:

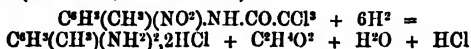


When a concentrated aqueous solution of (*p-o*)-tolylenediamine sulphate is mixed with a warm solution of an equivalent quantity of *potassium thiocyanate*, the solution then evaporated, the residue exhausted with alcohol, and the filtrate purified with animal charcoal and left to crystallise, a crystalline mass is obtained, which dissolves readily in water, and gives the thiocyanate reaction with ferric chloride. Hence the immediate product of the reaction is *tolylenediamine thiocyanate*, $(CN.S)^2C^6H^4$, but this salt soon changes, even without heating, into tolylenethiocarbamide, $(CS=N)^2C^6H^4$ (Lussy, *Ber.* vii. 1263).

With *furfural* in presence of an acid, this tolylenediamine forms a metallicly lustrous salt containing the elements of the two bodies *minus* the elements of water (H. Schiff, *Ber.* xi. 830). (*p-o*)-Tolylenediamine reacts with salts of *paradiatolyldiazin* (azotoluene), so as to produce diamidoditolyldiazin, or the chrysoïdine of the toluene series, $C^6H^3N^4 = C^6H^2.N=N.C^6H^3(NH^2)^2$, which crystallises in stellate groups of orange-yellow needles melting at 183°, easily soluble in alcohol and ether, nearly insoluble in water. Its salts crystallise more readily than those of chrysoïdine. The *platinchloride* has a crimson colour (see CHRYSOÏDINE, p. 470).

PARA-META-TOLYLENEDIAMINE, $C^6H^3.NH^2.NH^2.H^2$ (also called *Ortho-tolylenediamine*), is obtained by reduction of *m*-nitro-*p*-toluidine (vi. 1180), also

together with acetic acid, by reduction of *m*-nitro-*p*-trichloracetoluide with tin and hydrochloric acid (Friederici, *Ber.* xi. 1970):



This base melts at 89°. When treated in very dilute aqueous solution containing sulphuric acid, with a dilute solution of *potassium nitrite*, it is converted into a mid-

azototylene or amidotolylene-diazin, $\text{C}^6\text{H}^4\text{N}^2 = \text{NH}^2.\text{C}^6\text{H}^4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ || \\ \text{N} \end{smallmatrix}$, which crystal-

lises from toluene in large prisms containing 118 per cent. toluene of crystallisation, melts at 83°, and distils almost without decomposition at 323° (Ladenburg, *Ber.* ix. 219).

Reaction of (p-m)-Tolylenediamine with Aldehydes.—The combination of 1 mol. (*p-m*)-tolylenediamine and 2 mol. of an aldehyde, with elimination of 1 mol. water, gives rise to a class of bodies called tolualdehydines, which have been prepared and examined by Ladenburg (*Ber.* xi. 590, 1656).

Tolubenzaldehyde, $\text{C}^{21}\text{H}^{18}\text{N}^2$, is prepared by heating the diamine with benzaldehyde at 140°, and may also be obtained by heating the hydrochloride of the diamine with benzaldehyde, first at 100° and then at 130°, till hydrochloric acid ceases to be evolved. The crude product is dissolved in hot dilute hydrochloric acid, and the crystals which separate on cooling are decomposed by ammonia. The free base is soluble in alcohol, acetone and acids, and is deposited from an alcoholic solution, in transparent, monoclinic prisms which melt at 195.5°. In small quantities it sublimes without decomposition. The *hydrochloride*, $\text{C}^{21}\text{H}^{18}\text{N}^2.\text{HCl}.\text{H}^2\text{O}$, is but slightly soluble in strong hydrochloric acid, and separates out in long, needle-shaped crystals from a solution in the hot dilute acid.

Tolubenzaldehyde Ethiodide.—Two kinds of crystals are produced by the union of ethyl iodide with the aldehydine, viz., thick prisms or tables, and long needles, both of which are soluble in water and in alcohol; they have the same composition, $(\text{C}^{21}\text{H}^{16}\text{N}^2.\text{C}^2\text{H}_5\text{I}_2.\text{H}^2\text{O})$, and melt at 180°–181°. An alcoholic solution of iodine converts this compound into $\text{C}^{23}\text{H}^{22}\text{N}^2\text{I}_2$, which crystallises in brown plates melting at 123°. By the action of silver oxide on tolubenzaldehyde ethiodide an oily liquid is formed, the hydrochloric acid solution of which gives with platinum chloride a yellow crystalline precipitate of *tolubenzaldehyde ethylplatinochloride*, $(\text{C}^{23}\text{H}^{22}\text{N}^2\text{Cl})_2.\text{PtCl}_4$. *Tolubenzaldehyde Methiodide*, $\text{C}^{21}\text{H}^{18}\text{N}^2.\text{C}^1\text{H}_3\text{I}$, forms white needle-shaped crystals which melt with decomposition at 209°.

Tolubenzaldehyde oxidised with potassium permanganate yields an acid which melts at 253.5°–254.5°, and probably consists of *dibenzylideneamidobenzoic acid*,



Tolufurfuraldehyde, $\text{C}^{17}\text{H}^{14}\text{N}^2\text{O}^2$, obtained by heating (*p-m*)-tolylenediamine with furfural on the water-bath—or better by the action of furfural on the hydrochloride of (*p-m*)-tolylenediamine—crystallises in white silky prisms melting at 128.5°, easily soluble in ether, alcohol, benzene, and toluene, sparingly in ligroin. The *nitrate* crystallises in needles; the *platinochloride* forms yellow crystals easily soluble in alcohol; the *sulphate* crystallises from alcohol in prisms.

Tolufurfuraldehyde methiodide, $\text{C}^{17}\text{H}^{14}\text{N}^2\text{O}^2.\text{CH}_3\text{I}$, obtained by treating the aldehydine with excess of methyl iodide, crystallises in brilliant laminæ having a bitter taste, very sparingly soluble in cold water, slightly more soluble in alcohol, and melting at 195.5°. The corresponding *chloride* forms colourless shining laminæ easily soluble in water, and very poisonous; the *platinochloride* is a yellow powder. On adding an alcoholic solution of iodine to an alcoholic solution of tolufurfuraldehyde methiodide, a tri-iodide, $\text{C}^{19}\text{H}^{17}\text{N}^2\text{O}^2\text{I}_3$, is formed as a yellow-brown crystalline precipitate, and crystallises from hot alcohol in light-brown needles melting at 126°–128°. The alcoholic filtrate mixed with excess of iodine-solution deposits the *pentiodide*, $\text{C}^{19}\text{H}^{17}\text{N}^2\text{O}^2\text{I}_5$, in steel-blue oblique prisms melting at 100°.

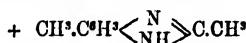
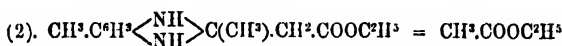
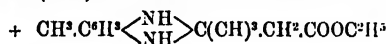
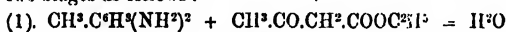
Tolu-anisaldehyde, $\text{C}^{23}\text{H}^{22}\text{N}^2\text{O}^2$, is prepared by adding anisaldehyde to a dilute aqueous solution of (*p-m*)-tolylenediamine hydrochloride, with addition of a little alcohol, and may be separated from the hydrochloride by ammonia and purified by crystallisation from alcohol. It forms stellate groups of needles, very soluble in alcohol and chloroform, sparingly in light petroleum, melting at 152°–156°.

(*p-m*)-Tolylenediamine and *Salicylaldehyde*, heated together at 110°, yield, not an aldehydine, but condensation-products, formed by combination of 1 mol. of the diamine and 3 mol. salicylaldehyde, with elimination of 3 mol. water, or of 2 mol. diamine and 3 mol. aldehyde, with elimination of 3 mol. water. The former com-

compound, $C^{12}H^{12}N^2O^2$, crystallises from alcohol in stellate groups of needles which melt at 106° - 110° , and are converted by long boiling with hydrochloric acid into an amorphous body which dissolves in potash-ley, forming a blue fluorescent liquid from which it is precipitated by carbonic acid. The second body, $C^{12}H^{12}N^2O^2$, called *azurine*, is obtained by heating the diamine with twice its weight of the aldehyde, at 135° , and treating the product with hot dilute hydrochloric acid. The acid solution is filtered; the white amorphous precipitate thrown down on adding strong hydrochloric acid to the filtrate is dissolved in alcoholic potash and shaken up with ether; the ethereal solution is evaporated to dryness; and the residue is dissolved in water, precipitated by carbon dioxide, and recrystallised from amyl alcohol. Azurine is characterised by the blue fluorescence of its solutions, and forms colourless tabular crystals soluble in amyl alcohol and acetone, melting at 250.5° .

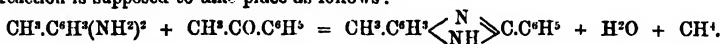
Methenyl-tolylenediamine, $C^8H^8N^2 = C^7H^7 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{CH}$, formed by prolonged heating of *p-m*-tolylene-diamine with formic acid, passes over on distillation at a very high temperature, and solidifies to a crystalline mass melting at 101° ; it has not, however, been obtained quite pure. Its *hydrochloride* is very soluble. The *platinochloride*, $(C^8H^8N^2.HCl)^2PtCl_4$, crystallises from water in yellow prisms (Ladenburg, *Ber.* x. 1123).

Ethenyl-tolylenediamine, $C^8H^{10}N^2 = C^7H^7 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} C.CH^3$, is formed on mixing ethylic acetoacetate and *p-m*-tolylene-diamine in molecular proportions. The temperature of the mixture sinks whilst the diamine dissolves, but afterwards rises, water then separating out, and the mixture solidifying to a crystalline mass (m. p. 82°), which has the composition $C^{12}H^{18}N^2O$, and when heated to 116° splits up into ethyl acetate and ethenyl-tolylenediamine melting at 198° - 199° . The reaction takes place by two stages as follows:



(Ladenburg a. Rugheimer, *Ber.* xii. 951).

Benzenyl-p-m-tolylenediamine, $C^{11}H^{12}N^2 = CH^3.C^6H^5 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} C.C^6H^5$.—To prepare this compound, a flask containing a mixture of *p-m*-tolylene-diamine and acetophenone in molecular proportions is gradually heated in an oil-bath to 180° , at which temperature it is kept for thirty-six hours, the loss of acetophenone by volatilisation being made up by dropping in small quantities from time to time. The reaction is supposed to take place as follows:



On exhausting the product with hydrochloric acid, a solution is obtained which, on cooling, deposits needle-shaped crystals of the hydrochloride of benzenyl-*p-m*-tolylene-diamine. The free base melts at 240° , and is identical in its properties with the anhydro-base which Kelbe obtained from mononitrobenzotoluide (p. 2002) (Ladenburg a. Rugheimer, *loc. cit.*)

Phthalyltolylene-diamines (R. Biedermann, *Ber.* x. 1160).—*Monophthalyltolylene-diamine*, $C^7H^5 \begin{smallmatrix} \text{NH.CO} \\ \text{NH.CO} \end{smallmatrix} C^6H^4$, and *Diphthalyltolylene-diamine*, $C^7H^5 \begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C^6H^4$, are formed by heating (*p-o*)-tolylene-diamine with phthalic anhydride, with or without addition of phosphoric anhydride, strong sulphuric acid, sodium acetate, or strong alcohol; also by the action of phthalyl chloride on tolylenediamine hydrochloride.

The *monophthalyl-base* crystallises in needles having a golden-yellow colour and silky lustre, and is best purified by repeated crystallisation from nitrobenzene. It melts at 192° , and is only very slightly soluble in hot water, but dissolves readily in hot alcohol and glacial acetic acid. Dilute hydrochloric acid at the boiling heat converts this substance into diphthalyltolylene-diamine and a base, $C^7H^5 \begin{smallmatrix} \text{N} \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C^6H^4$, represented by the constitutional formula $C^7H^5(NH.CO.C^6H^4.CO.NH.C^6H^4.NH^2)^2$. This base is easily soluble in water, and is resolved by repeated evaporation with hydro-

chloric acid into phthalic acid and (*p-o*)-tolylenediamine. Its hydrochloride is easily soluble, crystallises in rhomboïdal laminae, and forms a reddish-yellow platinumchloride, $C^8H^8N^2O^4 \cdot 2HCl, PtCl^4$.

Diphthalyltolylenediamine, $C^{21}H^{14}N^2$, is quite insoluble in water and in alcohol, and separates from solution in glacial acetic acid, in small shining crystals melting at 232° – 233° . It resists the action of hydrochloric acid, but is gradually decomposed by hot soda-ley.

(*m-o*)-Tolylenediamine (m. p. 80°) yields a monophthalyl-derivative melting at 104° , and a diphthalyl-derivative melting at 272° . Both are colourless.

(1–0) **Hydroxytoluenes**, $C^6H^4(CH^3).OH$. *Tolyl Alcohols*.—Cresols (pp. 582, 1540). From the results of Tiemann a. Schotten's experiments on the conversion of cresols into hydroxytoluic aldehydes (p. 2027), it appears that coal-tar cresol is a mixture of the three isomeric cresols, *ortho*-, *meta*-, and *para*. The three cresols are also present together in horse-urine in the form of sulphonic acids, and are produced by the dry distillation of vegetable matters: hence it may be inferred that they are produced in the one case as in the other by decomposition of the same plant-constituent (C. Preusse, *Zeitschr. physiol. Chem.* ii. 355). A cresol (modification not stated) is formed by oxidation of toluene in presence of aluminium chloride (Friedel a. Crafts, *Compt. rend.* lxxvi. 884).

According to Baumann a. Herter (*Ber.* ix. 138), cresol (commercial, or prepared from horse-urine), when given to animals in their food, is converted in the organism into a cresol sulphonic acid, which is eliminated in the urine.

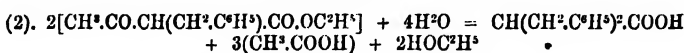
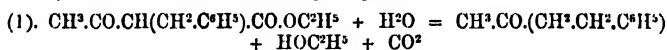
On the reaction of Cresols with *chloroform* and *sodium hydroxide*, see HYDROXY-TOLUIC ALDEHYDES (p. 2027).

On their reaction with *potassium chlorate* and *hydrochloric acid*, see TOLUQUINONES.

(0–1) **Hydroxytoluene**, or **Benzyl Alcohol**, $C^6H^5.CH^2OH$. When *berm chloride* is passed into this alcohol, hydrogen chloride is evolved, and dibenzoyl, $C^{14}H^{14}$, is formed, together with benzyl chloride (Councler, *Ber.* x. 1655).

Benzyl Acetate treated with *sodium* is converted into the benzylic ether of hydrocinnamic or β -phenylpropionic acid (p. 1068). In like manner *benzyl butyrate*, $CH^3.CH^2.CH^2.COO.CH^2.C^6H^5$, is converted by the action of sodium into the benzylic ether of normal phenylvaleric acid, $C^6H^5(CH^2)^4.COO.CH^2.C^6H^5$, which boils at 250° and yields phenylvaleric acid melting at 78° (Conrad a. Hodgkinson, x. 254).

Ethylic Benzylacetoacetate (pp. 14, 317) is converted by saponification partly into methyl-phenylethyl ketone, $CH^3.CO.(CH^2.CH^2.C^6H^5)$, partly into dibenzylacetic acid, $(C^6H^5.CH^2)^2.CH.COOH$, and acetic acid, perhaps thus:



(L. Ehrlich, *Liebig's Annalen*, clxxxvii. 11).

Parabromobenzyl-compounds (Jackson a. Lowery, *Ber.* x. 1209).—The *alcohol*, $C^6H^4Br.CH^2OH$, is most easily prepared by boiling parabromobenzyl bromide (p. 314) with water for some days, in a flask with reversed condenser. It is also obtained by heating parabromobenzyl acetate to 150° with aqueous ammonia. It forms long, colourless, elastic, flat needles, having a fine nacreous lustre and unpleasant odour, melting at 69° , and dissolving easily in boiling water, alcohol, ether, benzene, and carbon bisulphide.

The *acetate*, formed by heating the bromide with sodium acetate in alcohol, decomposes when distilled, and has not yet been obtained pure.

The *cyanide*, $C^6H^4Br.CH^2CN$, obtained by boiling the bromide with alcoholic solution of potassium cyanide, is a crystalline body of strong disagreeable odour, melting at 46° , and dissolving easily in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, but not in water. Heated at 100° with hydrochloric acid in sealed tubes, it is converted into parabromalphenatoluic acid, $C^6H^4Br.CH^2.COOH$; see TOLUIC ACIDS (p. 2026).

The *thiocyanate*, $C^6H^4Br.CH^2SCN$, formed by boiling the bromide with potassium thiocyanate, crystallises in needles, melting at 25° , and dissolving very easily in alcohol.

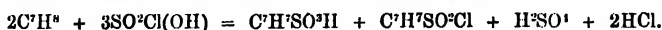
Orthobromobenzyl-compounds (Jackson a. Field, *Ber.* xiii. 1218).—The *bromide*, $C^6H^4Br.CH^2Br$, obtained by the action of bromine on boiling bromotoluene, is purified by distillation in vapour of hydrobromic acid; it crystallises in broad tablets melting at 30° . The *alcohol*, $C^6H^4Br.CH^2OH$, is produced by the action of

aqueous ammonia at 160° in a sealed tube, or of alcoholic potash on the acetate (formed from the bromide by means of alcoholic sodium acetate); also by boiling the bromide for several days with water. It crystallises from hot water, or better from ligroin, in needles melting at 80°; sublimes readily, and distils with vapour of water. By potassium permanganate it is oxidised to *o*-bromobenzoic acid. The cyanide prepared from the bromide with alcoholic potassium cyanide, is, in the crude state, a dark-coloured oil. Heated with hydrochloric acid in a sealed tube at 130°, it is converted into bromophenylacetic acid, $\text{C}^6\text{H}^4\text{Br}\cdot\text{CH}^2\text{COOH}$, melting at 102·5°–103° (see TOLUIC ACIDS, p. 2027). The thiocyanate, $\text{C}^6\text{H}^4\text{Br}\cdot\text{CH}^2\text{SCN}$, is an oil which does not solidify in a freezing mixture.

***p*-Chlorobenzyl-compounds.**—The chloride, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{H}\cdot\text{H}\cdot\text{Cl}\cdot\text{H}^2$, forms long white shining needles melting at 29°, having a pleasant aromatic odour, and acting strongly on the mucous membranes. It is very volatile, sublimes readily, dissolves easily in hot alcohol, also in ether, benzene, carbon sulphide, and glacial acetic acid. The bromide, $\text{C}^6\text{H}^4\text{Cl}\cdot\text{CH}^2\text{Br}$, prepared from *p*-chlorotoluene, melts at 48·5°, and boils at 225°–230°. Di-*p*-chlorobenzyl bromide boils at 280°–290°; the corresponding chloride at 288°. Tri-*p*-chlorobenzyl chloride boils at 196° (Jackson & Field, *Ber.* xi. 904). Beilstein & Kuhlberg (*Liebig's Annalen*, cl. 286), by treating trichlorotoluene with chlorine at the boiling heat, obtained a trichlorobenzyl chloride boiling at 273° (vi. 282).

***p*-Iodobenzyl-compounds.**—The bromide, $\text{C}^6\text{H}^4\text{Br}\cdot\text{H}\cdot\text{H}\cdot\text{I}\cdot\text{H}^2$, formed by heating *p*-iodotoluene in bromine-vapour, best between 115° and 150°, crystallises in white flat needles having an aromatic odour, and attacking the mucous membranes; it melts at 78·75°, sublimes in needles, is insoluble in water, but dissolves readily in hot alcohol, ether, benzene, and carbon sulphide. The alcohol, $\text{C}^6\text{H}^4\text{OH}\cdot\text{H}\cdot\text{H}\cdot\text{I}\cdot\text{H}^2$, prepared from the bromide by boiling with water, or from the corresponding acetate by means of aqueous ammonia, crystallises from carbon sulphide in white scales having a silky lustre and unpleasant odour; it melts at 71·75°; dissolves readily in alcohol, ether, benzene, and carbon sulphide. The cyanide, $\text{C}^6\text{H}^4\text{I}\cdot\text{CH}^2\text{CN}$, prepared from the bromide, crystallises in white nacreous plates melting at 50·5°, insoluble in water, easily soluble in alcohol, ether, carbon sulphide, and benzene. Heated at 100° with fuming hydrochloric acid, it is converted into iodophenylacetic acid, $\text{C}^6\text{H}^4\text{I}\cdot\text{CH}^2\text{COOH}$ (see *α*-TOLUIC ACID). The thiocyanate, $\text{C}^6\text{H}^4\text{I}\cdot\text{CH}^2\text{SCN}$, is obtained from the bromide by means of potassium thiocyanate, as an oil which gradually solidifies, but after purification by crystallisation from alcohol, it forms long white shining plates melting at 40°. It has a disagreeable odour, is moderately soluble in hot alcohol, easily in ether, benzene, carbon sulphide, and glacial acetic acid (Mabery & Jackson, *Ber.* xi. 55).

TOLUENESULPHONIC ACIDS, $\text{C}^6\text{H}^4(\text{CH}^3)\text{SO}^3\text{H}$. The three toluenesulphonic acids (*o*-, *m*-, and *p*-) are formed, together with the corresponding chlorides, by treating toluene (1·12 pt.) cooled to 10° with sulphuric hydroxychloride (2·8 pts.), the reaction taking place according to the following equation:



The best mode of proceeding is to pour the toluene by successive portions into the cooled sulphuric hydroxychloride. The mixed sulphonic chlorides may be separated from the rest of the product by pouring the whole into ice-cold water; and on cooling these mixed chlorides to –20°, the *para*-compound separates in the solid state, while the *ortho*- and *meta*-compounds remain liquid. These chlorides may be converted into the corresponding amides, which may be separated by fractional crystallisation. Toluene-*para*-sulphonic acid is obtained from the corresponding chloride, purified by crystallisation from ether, by boiling it with water; the *ortho*- and *meta*-acids by heating the corresponding amides with hydrochloric acid, the former at 135°–140°, the latter at 150° (Claesson & Wallin, *Ber.* xii. 1848).

The table on p. 2008 exhibits the properties of several salts of the three acids thus prepared, and of the corresponding amides.

The three toluenesulphonic acids are also produced by the action of sulphurous acid on the corresponding diazo-compounds (F. Müller & Wiesinger, *Ber.* xii. 1348). The *meta*-acid is further obtained by debromination of the *p*-bromotoluene-*m*-sulphonic acid, $\text{CH}^3 : \text{SO}^3\text{H} : \text{Br} = 1 : 3 : 4$, produced by the action of fuming sulphuric acid at 160°–180° on *p*-bromotoluene; also by dechlorination of the orthochlorotoluenesulphonic acid described by Hübner & Majert (p. 2013).

The following salts and derivatives of the *meta*- and *ortho*-sulphonic acids are described by Hübner & Post (*Liebig's Annalen*, clxix. 1–69), the description of the salts differing in several instances from those given by Claesson & Wallin.

Para	Meta	Ortho
$C^6H^7SO^3H + H^2O$. Crystallises better than the isomerides. Long thick leaflets, or flat prisms. Deliquescent.	$C^6H^7SO^3H + H^2O$. Thin crystalline scales. Very soluble and deliquescent.	$C^6H^7SO^3H + 2H^2O$. Thin leaflets. Very easily soluble. Deliquescent.
$C^6H^7SO^3K + H^2O$. Long prisms, like nitre. Soluble.	$C^6H^7SO^3K + H^2O$. Needles or thin plates, united to form nodules. Very easily soluble.	$C^6H^7SO^3K + H^2O$. Tables of rhombic or almost quadratic habit. Soluble.
$C^6H^7SO^3Na + 3H^2O$. Rectangular plates; easily soluble.	$C^6H^7SO^3Na + H^2O (?)$ Long leaflets, very soluble.	$C^6H^7SO^3Na + H^2O$. Plates, easily soluble.
$C^6H^7SO^3Ag$. Long plates, easily soluble.	$C^6H^7SO^3Ag$. Long leaflets, very soluble.	$C^6H^7SO^3Ag$. Plates, easily soluble.
$(C^6H^7SO^3)^2Ca + 4H^2Q$. Crystallises well in apparently monoclinic prisms. Easily soluble.	$(C^6H^7SO^3)^2Ca + 3H^2O$. Long fine needles; very easily soluble.	$(C^6H^7SO^3)^2Ca$. Separates from its solutions on cooling, in leafy crystals.
$(C^6H^7SO^3)^2Ba + H^2O$. Tufts of slender needles. 1 pt. dissolves in 4.8 pts. water at 12° .	$(C^6H^7SO^3)^2Ba + H^2O$. Crystallises indistinctly. 1 pt. in 4.4 water at 12° .	$(C^6H^7SO^3)^2Ba + H^2O$. Thin laminae. 1 pt. in 26 water at 12° .
$(C^6H^7SO^3)^2Pb$. Long needles, moderately soluble.	$(C^6H^7SO^3)^2Pb + 3H^2O$. Rectangular plates, easily soluble.	$(C^6H^7SO^3)^2Pb + H^2O$. Crystalline scales, sparingly soluble.
$(C^6H^7SO^3)^2Mg + 6H^2O$.	$(C^6H^7SO^3)^2Mg + 8H^2O$.	$(C^6H^7SO^3)^2Mg + 7H^2O$.
$(C^6H^7SO^3)^2Zn + 6H^2O$. Four-sided pointed prisms.	$(C^6H^7SO^3)^2Zn + 7H^2O$. Rectangular leaflets.	$(C^6H^7SO^3)^2Zn + 7H^2O$. Large prisms.
$(C^6H^7SO^3)^2Cd + 6H^2O$. Large rectangular plates.	$(C^6H^7SO^3)^2Cd + 5H^2O$. Small oblique-angled plates.	$(C^6H^7SO^3)^2Cd + 2H^2O$. Small rectangular plates, very soluble.
$(C^6H^7SO^3)^2Mn + 6H^2O$. Large rectangular plates.	$(C^6H^7SO^3)^2Mn + 7H^2O$. Plates, or radiating tufts.	$(C^6H^7SO^3)^2Mn + 2H^2O$. Square plates.
$(C^6H^7SO^3)^2Cu + 6H^2O$. Needles and oblique-angled plates.	$(C^6H^7SO^3)^2Cu + 4H^2O$. Leaflets.	$(C^6H^7SO^3)^2Cu + 4H^2O$. Six-sided leaflets.
$C^6H^7SO^3NH^2$. Crystallises from water and alcohol in leaflets. Sparingly soluble in water; more so in alcohol. 1 pt. amide in 515 pts. of water at 4° , or in 13.5 pts. of alcohol at 5° . M. p. 136° .	$C^6H^7SO^3NH^2$. Crystallises from alcohol and water in long, leafy forms. Sparingly soluble in water; more so in alcohol. 1 pt. amide in 248 pts. water at 9° , or in 5.7 pts. of alcohol at 5° . M. p. 107° - 108° .	$C^6H^7SO^3NH^2$. From water and alcohol in quadratic octohedrons and prisms. Insoluble in cold water; sparingly soluble in alcohol. 1 pt. amide in 958 pts. water at 9° , or in 28 pts. of alcohol at 5° . M. p. 153° - 154° .

Toluenemetasulphonic acid, $C^6H^5.H.SO^2H.H^2$. — The *barium salt*, $[C^6H^4(CH^3)SO^2]^2Ba + 2H^2O$, is very soluble in water and alcohol, and forms a crystalline powder. The *lead salt*, $[C^6H^4(CH^3)SO^2]^2Pb + 2H^2O$, crystallises from a concentrated aqueous solution in thin plates grouped in rosettes, and from absolute alcohol in long needles. The *calcium salt*, $[C^6H^4(CH^3)SO^2]^2Ca$, is very soluble in water. On heating a concentrated alcoholic solution, the salt separates in small glistening plates, which redissolve on cooling. The *sodium salt*, $C^6H^4(CH^3)SO^2Na + \frac{1}{2}H^2O$, is very soluble in water, and crystallises from absolute alcohol in large shining plates. The *potassium salt*, $C^6H^4(CH^3)SO^2K + \frac{1}{2}H^2O$, is a similar compound, crystallising from alcohol in plates resembling naphthalene.

Metatoluenesulphonic chloride, $C^6H^4(CH^3)SO^2Cl$, is a limpid pale-yellow liquid, having a penetrating smell. It does not solidify at -10° , and is not decomposed by water even at 130° . Ammonia converts it into $C^6H^4(CH^3)SO^2NH^2$, crystallising from water at 40° in large plates, and at 20° in thin needles melting at $90^\circ-91^\circ$.

Metatolyl sulphydrate, $C^6H^4(CH^3)SH$, is formed by acting with tin and hydrochloric acid on the chloride. It is a heavy refractive liquid, having a powerful smell, and attacking the skin. Boiling dilute nitric acid converts it into the disulphide, $[C^6H^4(CH^3)S^2]$, an oily liquid boiling at about 150° .

Toluenearthosulphonic acid, $C^6H^3.SO^2H.H^4$, obtained by the action of water and sodium-amalgam on β -parabromotoluenesulphonic acid, forms very soluble salts. The *lead salt*, $(C^6H^3SO^2)^2Pb + 4H^2O$, crystallises in needles. The *barium salt*, $(C^6H^3SO^2)^2Ba + 4H^2O$, and the *potassium salt*, $C^6H^3SO^2K + H^2O$, form monoclinic plates; the anhydrous *sodium salt* crystallises in needles. The *chloride*, $C^6H^3SO^2Cl$, is an oily liquid. The *amide*, which is freely soluble in water, alcohol, and ether, crystallises in monoclinic plates melting at $152^\circ-153^\circ$.

Orthotolyl Sulphydrate, $C^6H^3.SH.H^4$, prepared by treating the chloride of the brominated acid just described with tin and hydrochloric acid, and the resulting bromotolyl sulphydrate with sodium-amalgam and alcohol, crystallises from alcohol in soft glistening plates insoluble in water. Its *lead salt*, $[C^6H^4(CH^3)S]^2Pb$, is a bright brick-red precipitate which readily absorbs oxygen and turns white (Hübner a. Post).

Tolueneparasulphonic acid, $C^6H^3.H.H.SO^2H.H^2$, is converted by fusion with sodium formate into paratoluic acid, the reaction being similar to that by which terephthalic acid is formed from parasulphobenzonic acid: $C^6H^3.SO^2H + ClHNaO^2 = C^6H^3O^2 + SO^2HNa$. The yield is small, but paratoluic acid is the only product (Remsen, Ber. viii. 1412).

Toluenedisulphonic Acids, $C^6H^3(SO^2H)^2.CH^3$. The table on p. 2010 exhibits a comparison of the properties of the α - and β -disulphonic acids obtained by Hakansson, and the γ -acid by Senhofer (vii. 1170, 1171).

Gnehm a. Ferrer prepare (Ber. x. 542) toluenedisulphonic acid by adding 1 pt. of toluene by small portions to 3 or 4 pts. of sulphuric anhydride melted in a capacious flask by means of hot water; then heat the mixture to $150^\circ-180^\circ$ for two hours, and ultimately for a short time at 200° . The dark syrupy liquid thus formed contains a disulphonic acid which appears to be identical with Hakansson's α -acid. The same acid is formed on passing the vapour of toluene into sulphuric acid heated to 240° .

Bromotoluenesulphonic Acids, $C^6H^3Br(SO^2H)CH^3$ (Hübner a. Post, Liebig's Annalen, clxix. 1-69). (1). Parabromotoluene dissolved in fuming sulphuric acid, either at a temperature not exceeding 80° or at $160^\circ-180^\circ$, yields two monosulphonic acids, distinguished as α and β , the constitution of which is as follows:

	CH ³	SO ² H	Br
α -acid	1	3	4
β -acid	1	2	4

The two acids may be separated by recrystallisation of their barium salts, that of the α -acid being much more soluble than the β -salt.

α -Parabromotoluenesulphonic acid is a very soluble, crystalline laminated mass. The *barium salt*, $[C^6H^3Br(CH^3)SO^2]^2Ba + 7H^2O$, forms colourless, well-defined, long and compact rhombic needles. The *lead salt*, $[C^6H^3Br(CH^3)SO^2]^2Pb + 3H^2O$, is obtained from a concentrated solution in long needles, which, when recrystallised from a dilute solution, are converted into small, light yellow, compact rhombic plates. The *strontium salt*, $[C^6H^3Br(CH^3)SO^2]^2Sr + 7H^2O$, crystallises in hard, four-sided pyramids.

The α -amide, $C^6H^3Br(CH^3)SO^2NH^2$, obtained by treating the impure chloride of the acid with solid ammonium carbonate, and then adding concentrated ammonia, dissolves sparingly in cold water, freely in alcohol, ether, and hot water, and crystallises in long, soft, silky needles, melting at $151^\circ-152^\circ$.

	α -Acid	β -Acid	γ -Acid
Free acid . .	Viscid; bears a heat of more than 100° without decomposition.		Viscid, mixed with crystals; decomposed at the heat of a water-bath.
Potassium salt .	Firmly coherent crusts; crystals with faces curved like a weaver's shuttle; containing 1 mol. H ² O, which is scarcely given off at 160°, certainly not at 110°.	Nodular groups of microscopic crystals.	Short, well-defined prisms containing 1 mol. H ² O; giving off water and becoming opaque on exposure to the air.
Ammonium salt .	Beautiful limpid six-faced prisms or tablets, containing 1 mol. H ² O.	Small thin tablets.	Easily soluble needle-shaped crystals, often appearing crossed.
Barium salt.	Crystallises with difficulty in small prisms, containing at 17° 1.33 pt. water to 1 pt. salt; at ordinary temperatures 1½ to 2, at 100° 1 mol. water.	Indistinctly crystalline crusts, containing 1 mol. H ² O; the solution at 15° contains 11.66 pts. water to 1 pt. salt.	Easily soluble crystalline pulp; in the air-dried state it contains 3½ H ² O.
Cadmium salt .	Radio-crystalline mass, or long slender needles.	—	Easily soluble gummy mass.
Silver salt . .	Colourless, rather large crystals, with curved faces. The only anhydrous salt. Blackens slightly when exposed to light.	—	Yellow crystalline deposits, gradually blackening when exposed to light; contains 2 mol. H ² O; difficult to obtain in the anhydrous state.

α -Nitro-*p*-bromotoluenesulphonic acid, $C^6H^2Br(NO^2)(CH^3)SO^3H$, produced by adding the anhydrous barium salt to warm fuming nitric acid, crystallises in small, pale-yellow, deliquescent needles, and forms very soluble salts. Its *barium salt*, $[C^6H^2Br(NO^2)(CH^3)SO^3]^2Ba + H^2O$, separates by slow evaporation in thin yellow needles, and from a concentrated solution in crystals resembling sal-ammoniac. The *lead salt*, $[C^6H^2Br(NO^2)(CH^3)SO^3]^2Pb + 2\frac{1}{2}H^2O$, crystallises in colourless, glistening octahedrons, or sometimes in needles, which also contain water, but are more soluble in alcohol than the octahedrons. The *strontium salt*, $[C^6H^2Br(NO^2)(CH^3)SO^3]^2Sr + 5H^2O$, crystallises in thin, fan-shaped needles. The *sodium salt*, $C^6H^2Br(NO^2)(CH^3)SO^3Na$, forms long and very thin needles.

α -Parabromosulphobenzoic acid, is prepared by boiling potassium α -parabromotoluenesulphonate with a chromic acid solution. On concentrating the solution, the salt $C^6H^3Br(CO^2H)SO^3K + H^2O$ crystallises out in thin needles. The *barium salt*, $C^6H^3Br\left\{\begin{smallmatrix} CO^2 \\ SO^3 \end{smallmatrix}\right\}Ba + \frac{1}{2}H^2O$, crystallises in thin, glistening plates; the salts $C^6H^3Br\left\{\begin{smallmatrix} CO^2 \\ SO^3 \end{smallmatrix}\right\}Ca$, and $C^6H^3Br\left\{\begin{smallmatrix} CO^2 \\ SO^3 \end{smallmatrix}\right\}Pb + 2H^2O$ form small needles.

β -Parabromotoluenesulphonic acid is readily soluble in water and alcohol,

sparingly in ether, and forms a crystalline laminated mass. It is not converted into an isomeric modification by heating it to 210° . Its *barium salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Ba} + \text{H}_2\text{O}$, crystallises, when a dilute solution is slowly evaporated, in hard, compact plates, and from a concentrated solution in very thin and brilliant plates. If it be mixed with one of the isomeric salts, or with the calcium salt, it separates from a concentrated solution as a white powder. The *lead salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Pb} + 3\text{H}_2\text{O}$, crystallises in silky, stellar needles. The *calcium salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Ca} + 4\text{H}_2\text{O}$, is very soluble, and forms either thin, long rhombic needles, or compact plates. The *sodium salt*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{Na} + \text{H}_2\text{O}$, crystallises in thin, transparent, four-sided prisms. The *magnesium salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Mg} + 8\frac{1}{2}\text{H}_2\text{O}$ (?), forms soft, silky tufts, and $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Sr} + \text{H}_2\text{O}$ thin plates. The *copper salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Cu} + 7\text{H}_2\text{O}$, crystallises in large, pale-blue plates.

The *β -chloride*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{Cl}$, obtained by the action of phosphorus pentachloride on the acid or its sodium salt, crystallises from chloroform in plates, melting at about 35° , and having a peculiar smell.

The *β -amide*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{NH}_2$, crystallises from water in long, slender, glistening needles, melting at 166° – 167° .

β -Nitrobromotoluenesulphonic acid, $\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2\text{H}$, formed by adding dry β -parabromotoluenesulphonic acid to warm fuming nitric acid, crystallises from ether in deliquescent scales, having a very bitter taste. Its *barium salt*, $[\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2]_2\text{Ba} + 2\text{H}_2\text{O}$, crystallises in warty needles. The *lead salt*, $[\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2]_2\text{Pb} + 3\text{H}_2\text{O}$, separates from solution in ether-alcohol in thin, colourless needles. The *copper salt*, $[\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2]_2\text{Cu} + 6\text{H}_2\text{O}$, forms microscopic, four-sided green prisms. The *silver salt*, $\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2\text{Ag}$, is a precipitate consisting of glistening scales. The *strontium salt*, $[\text{C}^6\text{H}^2\text{Br}(\text{NO}^2)(\text{CH}^3)\text{SO}^2]_2\text{Sr} \cdot 7\text{H}_2\text{O}$, dissolves freely in water and alcohol, and forms small yellow needles. The *sodium salt* is very soluble, and could not be obtained in distinct crystals.

β -Parabromosulphobenzoic acid, $\text{C}^6\text{H}^3\text{Br}(\text{SO}^2\text{H})\text{CO}^2\text{H}$.—When β -parabromotoluenesulphonic acid is boiled with chromic acid mixture, a large portion is completely destroyed, while another is slowly oxidised to the corresponding benzoic acid, which forms a deliquescent mass, and yields very soluble salts. The barium and calcium salts consist of microscopic plates.

Orthobromotoluene-metasulphonic acid, $\text{CH}^3 : \text{Br} : \text{SO}^2\text{H} = 1 : 2 : 3$ or $1 : 2 : 5$.—Orthobromotoluene, gently heated with fuming sulphuric acid, yields only one sulphonic acid, the barium salt of which, when treated with sodium-amalgam, yields *meta*-toluenesulphonic acid: hence the constitution of the orthobromosulphonic acid must be represented by one of the formulæ above given, but the reactions hitherto studied do not enable us to decide between them. The salts of this acid crystallise well, and do not give off their water of crystallisation till heated above 100° ; only a few of them give it off over sulphuric acid. The *barium salt*, $[\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2]_2\text{Ba} + 2\text{H}_2\text{O}$, forms rhomboidal plates; the *strontium salt* is a very similar body. The *calcium salt* crystallises very slowly from a concentrated solution in compact rhombic six-sided plates containing $2\text{H}_2\text{O}$. The *lead salt* crystallises, with $2\text{H}_2\text{O}$, from very strong solutions in very thin small plates, and from a dilute solution in tufts of needle-shaped crystals. The *sodium salt*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, forms well-defined brilliant rhomboidal plates. The *potassium salt* crystallises, also with $\frac{1}{2}\text{H}_2\text{O}$, in plates or short thick white needles. The *copper salt* is very soluble, and crystallises in very thin light-coloured plates; the *zinc salt* in small glistening needles; the *magnesium salt* in small scales.

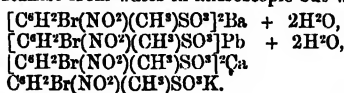
The *chloride*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{Cl}$, prepared by treating the dry sodium salt with phosphorus pentachloride, forms a crystalline mass, consisting of needle-shaped crystals, and having a pungent smell. It crystallises from ether in large plates, melting at 52° – 53° . It is but slowly acted upon by caustic soda or boiling water, dissolves sparingly in concentrated sulphuric acid, and without change in fuming nitric acid. At 250° it begins to boil, and at 260° it is decomposed into charcoal, sulphur dioxide, and $\text{C}^6\text{H}^3\text{BrCl}(\text{CH}^3)$. When heated with water at 200° for several days, it is reconverted into orthobromotoluene-sulphonic acid, no isomeric modification being formed.

The *amide*, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SO}^2\text{NH}_2$, is sparingly soluble in cold water, more freely in boiling water, very readily in alcohol and ether, and crystallises in long glistening needles, melting at 133° – 134° , and boiling, with decomposition, at about 290° .

Orthobromotolyl sulphhydrate, $\text{C}^6\text{H}^3\text{Br}(\text{CH}^3)\text{SH}$, is formed by boiling the chloride with tin and hydrochloric acid. It is a refractive limpid liquid, having a peculiar smell, and boiling with decomposition, but volatilising with steam. The lead salt is a bright yellow precipitate. On heating the sulphhydrate with dilute nitric acid, or

acting on the sodium salt with alcoholic iodine, the *disulphide*, $(C^6H^4Br(CH^3)S)^2$, is formed, crystallising from alcohol in small needles, and from a mixture of xylene and alcohol in long needles melting at 56° – 58° .

Orthobromonitrotoluenesulphonic acid is a deliquescent mass, readily soluble in alcohol and ether. The free acid, as well as its salts, has a very bitter taste. The following four salts crystallise from water in microscopic but well-defined crystals:



$C^6H^4Br(NO^2)(CH^3)SO^3Na + H^2O$ crystallises in tufts of long needles, and is less soluble in water than the preceding salts.

Orthobromosulphobenzoic acid, $C^6H^4Br(SO^3H)CO^2H$, was prepared by oxidising the barium salt of the corresponding toluenesulphonic acid with chromic acid solution. Its *potassium salt*, $C^6H^4Br(CO^2H)SO^3K + \frac{1}{2}H^2O$, crystallises from water in thin plates resembling naphthalene. The *barium salt*, $C^6H^4Br\left\{ \begin{smallmatrix} CO^2 \\ SO^3 \end{smallmatrix} \right\} Ba + 2H^2O$, separates, on adding alcohol to the concentrated solution, in tufts of glistening and very thin needles. When treated with sodium-amalgam it yields toluene-metasulphonic acid. The *lead salt*, $C^6H^4Br\left\{ \begin{smallmatrix} CO^2 \\ SO^3 \end{smallmatrix} \right\} Pb + 2H^2O$, forms small white glistening needles; the *calcium salt* is very soluble, and forms long silky needles.

Orthobromotolueneparasulphonic acid, $CH^3 : Br : SO^3H = 1 : 2 : 4$, is formed by the action of hydrobromic acid on the diazo-compound, $C^6H^4\left\{ \begin{smallmatrix} SO^3 \\ N=N \end{smallmatrix} \right\}$, produced by passing nitrous gas into a mixture of equal volumes of water and alcohol in which orthotoluidine-parasulphonic acid is suspended (p. 2017). Its *potassium salt*, $C^6H^4BrSO^3K$, forms nodular groups of microscopic very soluble needles. The *barium salt*, $(C^6H^4BrSO^3)^2Ba + 2H^2O$, crystallises in irregular microscopic plates, which dissolve sparingly in cold water, and do not give off their water over sulphuric acid. The *lead salt*, $(C^6H^4BrSO^3)^2Pb + 2\frac{1}{2}H^2O$, forms nodular masses without recognisable crystalline form. It dissolves sparingly in cold water, and gives off part of its crystallisation-water over sulphuric acid. The *chloride* melts at 54° ; the *amide* separates from hot water in microscopic prisms which melt at 151° , dissolve sparingly in water, easily in alcohol (Hayduck, *Liebig's Annalen*, clxxii. 206).

Nitro-orthobromotoluene-parasulphonic acid, $C^6CH^3.Br.NO^2.SO^3H.H.H$, or $C^6CH^3.Br.H.SO^3H.NO^2.H$, is formed by the action of hydrobromic acid on the nitro-diazotoluenesulphonic acid obtained by adding orthotoluidine-parasulphonic acid to cold fuming nitric acid (p. 2017); also by nitration of orthobromotoluene-*p*-sulphonic acid. It remains on evaporation as a compact mass of microscopic needles easily soluble in water and in alcohol. The *barium salt*, $[C^6H^4Br(NO^2)SO^3]^2Ba + 3H^2O$, crystallises in tufts of needles which have a satiny lustre, are sparingly soluble in cold, easily in hot water, and do not give off any water over sulphuric acid. The *chloride* crystallises in microscopic needles; the *amide*, $C^6H^4Br(NO^2)SO^2NH^2$, separates from alcohol in long needles easily soluble in water, sparingly in boiling alcohol. Both these compounds when heated decompose without previous fusion.

The nitro-acid is converted by *ammonium sulphide* into an amidorthobromotoluene parasulphonic acid—obtained, however, only in an impure and amorphous state—which is converted by sodium-amalgam into metatoluidine-parasulphonic acid, $CH^3 : NH^2 : SO^3H = 1 : 3 : 4$ (Hayduck).

Tribromotoluene-parasulphonic acid, $CH^3 : Br : Br : SO^3H : Br = 1 : 2 : 3 : 4 : 5$ or $1 : 2 : 3 : 4 : 6$, is obtained by evaporating diazotoluene-parasulphonic acid with hydrobromic acid, as a yellowish deliquescent mass. Its *barium salt*, $(C^6H^4Br^3SO^3)^2Ba + 1\frac{1}{2}H^2O$, crystallises in white nodules very slightly soluble in water; the *potassium salt*, $C^6H^4Br^3SO^3K$, in dazzling white needles, very soluble in hot, much less soluble in cold water. The *chloride* is an uncrystallisable viscid oil; the *amide*, a reddish non-crystalline powder, nearly insoluble in boiling water (Hayduck, *Liebig's Annalen*, clxxiv. 354).

Metabromotoluenesulphonic acid.—The action of sulphuric acid on metabromotoluene might give rise to four isomeric acids, viz., $CH^3 : Br : SO^3H = 1 : 3 : 2$, $1 : 3 : 4$, $1 : 3 : 5$, and $1 : 3 : 6$; and, according to Wroblewsky (vii. 1172), three of these are actually produced. Grete, on the other hand (*Ber.* vi. 790; viii. 565; *Liebig's Annalen*, clxxvii. 233), finds that this reaction gives rise to only one sulphonic acid, the salts of which exhibit the following characters:—The *barium salt*, $(C^6H^4BrSO^3)^2Ba$, crystallises in laminæ resembling naphthalene (Wroblewsky's

β -salt), the first and last crops of crystals being exactly alike. The *strontium salt*, $(C^7H^4BrSO^3)^2Sr + H^2O$, forms nodular groups of short triangular colourless laminae, hygroscopic in the anhydrous state. The *calcium salt*, $(C^7H^4BrSO^3)^2Ca + 2H^2O$, crystallises in large, transparent, shining, six-sided prisms, often flattened to long six-sided plates, which under the microscope are seen to be of rhombic form and very sharply defined. The anhydrous salt is scarcely at all hygroscopic. The *magnesium salt*, $(C^7H^4BrSO^3)^2Mg + 6H^2O$, crystallises in concentrically radiate groups of snow-white shining needles which do not give off their water till heated above 200° . It is very soluble and extremely hygroscopic. The *copper salt*, $(C^7H^4BrSO^3)^2Cu + 4H^2O$, forms pale blue rhombic tablets often grouped in rosettes. Its neutral solution has a fine green colour, and the solid salt, when dehydrated at 220° , acquires a splendid dark green colour changing to light green on cooling. At 250° it turns brown. The *lead salt*, $(C^7H^4BrSO^3)^2Pb + 3H^2O$, has the aspect of potassium chlorate, and appears under the microscope to consist of sharply defined tablets grouped in rosettes. The *potassium salt* is extremely soluble in water, and is precipitated from the solution by alcohol as an oily liquid which solidifies on trituration to a crystalline mass. When fused with potash it yields salicylic acid (Grote).

A *bromotoluenemetasulphonic acid* is formed by the action of alcohol under pressure on the diazo-compound $C^7H^4Br \begin{smallmatrix} SO^3 \\ \text{N=N} \end{smallmatrix}$ obtained from bromoparatoluidine-metasulphonic acid (p. 2021), and forms, after purification, a colourless crystalline mass. Its *potassium salt*, $C^7H^4BrSO^3K$, crystallises from a moderately dilute solution in fine prisms. The *barium salt*, $2(C^7H^4BrSO^3)^2Ba + 7H^2O$, forms long thick needles slightly soluble in cold water. The *lead salt*, $(C^7H^4BrSO^3)^2Pb + 3H^2O$, crystallises from hot water in groups of long needles, sparingly soluble in cold water. The *chloride* melts at 53° ; the *amide* at 134° (v. Pechmann, *Ber.* vii. 1718).

Chlorotoluenesulphonic Acids, $C^7H^4ClSO^3 = C^6H^4Cl(SO^3H).CH^3$. From the mixture of chlorotoluenes produced by passing chlorine into toluene in presence of iodine, Vogt u. Henniger obtained, by the action of fuming sulphuric acid, two isomeric chlorosulphonic acids (vii. 878, 1172), and more recently Hübner u. Majert (*Ber.* vi. 790) have in like manner obtained three chlorotoluenesulphonic acids, which may be separated by means of their barium salts.

Orthochlorotoluenesulphonic acid.—The *potassium salt* of this acid, $C^7H^4ClSO^3K + \frac{1}{2}H^2O$, crystallises in large colourless quadratic tables, truncated at the summits, and having a nacreous lustre; becomes anhydrous at 100° ; is more soluble than either of the three preceding salts. The *sodium salt* resembles the potassium salt in appearance and in its amount of water, but is more soluble. The *ammonium salt*, $C^7H^4ClSO^3NH^4 + H^2O$, forms rosettes of dull colourless needles. The *barium salt*, $(C^7H^4ClSO^3)^2Ba + 2H^2O$, forms small, somewhat elongated lozenge-shaped laminae, often with truncated summits, and usually grouped together by their narrow edges. They have a strong lustre when dried, and become anhydrous at 180° . The *calcium salt*, $(C^7H^4ClSO^3)^2Ca + 2H^2O$, forms radiate groups of long flat crystals, truncated at the ends. The *lead salt*, $(C^7H^4ClSO^3)^2Pb + 2H^2O$, forms rosettes of short compressed needles, truncated at the ends, and having a strong lustre. The *copper salt*, $(C^7H^4ClSO^3)^2Cu + \frac{1}{2}H^2O$, forms well-defined thick blue crystals of the regular system. The *cuprammonium salt* forms small regular crystals of a splendid dark blue colour.

This chlorotoluenesulphonic acid yields by oxidation an orthochlorosulphobenzoic acid, the *acid potassium salt* of which, $C^6H^4Cl(SO^3K)(CO^2H) + H^2O$, crystallises in felted groups of slender asbestos-like needles; the *normal barium salt*, $C^6H^4Cl(SO^3BaCO^2) + 2H^2O$, in indistinct stellate groups of small needles; and the *normal lead salt*, $C^6H^4Cl(SO^3PbCO^2) + 2H^2O$, in indistinct nodules.

By the action of *sodium-amalgam*, the orthochlorotoluenesulphonic acid is converted into toluenemetasulphonic acid (p. 2008). Hence its constitution must be $CH^3 : Cl : SO^3H = 1 : 2 : 3$ or $1 : 2 : 5$.

α -Parachlorotoluenesulphonic acid.—The *barium salt*, $(C^7H^4ClSO^3)^2Ba + \frac{1}{2}H^2O$, forms long pointed needles which on recrystallisation yield groups of small highly lustrous laminae with truncated summits. It dissolves in 7 pts. water at 14.5° . The *sodium salt*, $C^7H^4ClSO^3Na + 5H^2O$, forms long pointed needles, or small highly lustrous elongated quadrilateral crystals with truncated summits.

β -Parachlorotoluenesulphonic acid.—The *potassium salt*, $C^7H^4ClSO^3K + H^2O$, crystallises only from very strong solutions in delicate colourless needles having a silky lustre; it readily forms supersaturated solutions. The *barium salt*, $(C^7H^4ClSO^3)^2Ba + H^2O$, forms thick amber-yellow nodules or transparent crystalline crusts or colourless microscopic laminae. The *calcium salt*, $(6H^2O)$, forms rosettes of small truncated tables or small elongated efflorescent laminae. The *lead salt*, $(8H^2O)$,

forms rosettes of snow-white needles. The *copper salt*, $(7H^2O)$, forms large light blue brittle laminae. The *cuprammonium salt* forms crusts of small thick crystals having a deep indigo-blue lustre and efflorescing in the air.

The barium salts of the ortho- and of the β -parachlorosulphonic acid agree in crystalline form and amount of water with the corresponding salts of the brominated acids.

Iodotoluenesulphonic Acids. Paraiodotoluene, like the corresponding bromo-compound, when treated with sulphuric anhydride, yields two isomeric sulphonic acids.

β -*Paraiodotoluenesulphonic acid*, $C^6H^4(CH^3)I.SO^3H$, is prepared by very gradually mixing paraiodotoluene with the calculated quantity of sulphuric anhydride, both dissolved in chloroform. It is a colourless, deliquescent, crystalline mass, which does not give up any iodine to caustic soda-solution at 200° . Its *potassium salt*, $C^6H^4I.SO^3K + H^2O$, forms shining, very soluble laminae. The *sodium salt*, $C^6H^4I.SO^3Na + \frac{1}{2}H^2O$, forms dense aggregates of whetstone-like very soluble crystals. The *barium salt*, $\{C^6H^4I.SO^3\}_2Ba + H^2O$, crystallises in thin laminae: it is the least soluble of the salts of this acid. The *calcium salt*, $(+3H^2O)$, forms very soluble needles having a silky lustre; the *copper salt*, $(+6H^2O)$, light blue easily soluble needles. The *amide*, $C^6H^4I.SO^2NH_2$, forms colourless crystals, which melt at 178° . 179° , dissolve in hot water, and more readily in alcohol.

The barium salt of α -*Paraiodotoluenesulphonic acid* separates from the last mother-liquors of the β -salt after prolonged sojourn over sulphuric acid, in long, colourless, very soluble needles, which have the composition $(C^6H^4I.SO^3)_2Ba + 4H^2O$, and retain the same amount of water on recrystallisation (H. Glassner, *Ber.* viii. 560).

Nitrotoluenesulphonic Acids. *Paranitrotoluenesulphonic acid*, $C^6H^4.NO^2.SO^3H.H.NO^2.H^2$, which Beilstein a. Kuhlberg obtained by the action of fuming sulphuric acid on *p*-nitrotoluene (vii. 1173), crystallises from water in transparent, well-defined, rhombic fablets or prisms, which have the composition $C^6H^4(NO^2)SO^3H + 2\frac{1}{2}H^2O$, give off their water at 130° , and melt at 133.5° . From a solution strongly acidulated with sulphuric acid, it separates anhydrous, and then melts at 130° . It dissolves easily in water, alcohol, ether, and chloroform. 100 pts. of the aqueous solution contain 67.71 pts. of the hydrated acid at 23° and 71.45 pts. at 28° . The *barium* and *lead salts* have the composition assigned to them by Beilstein a. Kuhlberg; the latter, however, when dried over sulphuric acid or at 120° , gives off only $1\frac{1}{2}H^2O$, the rest ($\frac{1}{2}H^2O$) at 190° . The *potassium* and *ammonium salts* form long, slender, anhydrous needles. The *chloride*, $C^6H^4(NO^2)SO^2Cl$, crystallises from ether in rhombic tablets melting at 43° to 44.5° , dissolves readily in ether and in chloroform, sparingly in alcohol. The *amide*, $C^6H^4(NO^2).SO^2NH_2$, separates from aqueous solution in long brittle needles melting at 186° , sparingly soluble in alcohol, ether, and cold water, more readily in hot water, still more in ammonia. By reduction with hydrogen sulphide it yields the corresponding amido-acid (Jonsen, *Lieb. Ann.* clxxii. 230).

Hart a. Remsen (*Ber.* x. 1046), by treating paranitrotoluene with fuming sulphuric acid, obtained two isomeric mononitro-acids, separable by means of their calcium salts, the solution first depositing long needles having the composition $[C^6H^4(NO^2)SO^3]_2Ca + 4H^2O$, and afterwards, together with these, large monoclinic prisms containing $6H^2O$, which retained their form on recrystallisation. Which of these two salts is derived from Beilstein a. Kuhlberg's acid is a point not yet determined.

Dinitrotoluenesulphonic Acids, $C^6H^2(NO^2)_2(SO^3H).CH^3$ (H. Schwanert, *Lieb. Ann.* clxxxvi. 342; *Ber.* x. 28). When a mixture of toluene and fuming sulphuric acid, which contains *p*- and *o*-toluenesulphonic acids—or a mixture of toluene, fuming sulphuric acid, and strong nitric acid, which contains *o*-nitrotoluene-*p*-sulphonic acid (in excess) and *p*-nitrotoluene-*o*-sulphonic acid—is boiled for some time with strong nitric acid, two dinitrotoluenesulphonic acids are produced. The dinitrotolueneorthosulphonic acid produced from the *o*-nitrotoluene-*p*-sulphonic acid—and therefore the more abundant of the two—is easily purified by means of the sparing solubility of its barium salt; less easy to purify is the dinitro-acid obtained from paranitrotoluene-ortho-sulphonic acid, the barium salt of which is a pale-yellow, easily soluble, granular mass, having, when dried over sulphuric acid, the composition $[C^6H^4(NO^2)_2SO^3]_2Ba + 4H^2O$.

Dinitrotoluene-para-sulphonic acid, the only one of the two which has yet been exactly investigated, is prepared as follows: To a cooled mixture of 200 g. toluene with an equal volume of fuming sulphuric acid is added, at first by drops, about 1 kg. nitric acid of sp. gr. 1.5; the mixture is heated in a retort as long as red fumes are given off; and the distillate is then poured back, this treatment being

repeated five or six times, and finally the nitric acid is distilled off as completely as possible. The residual liquid, which solidifies on cooling, is mixed with twice its volume of water, which separates a small quantity of dinitrotoluene; the liquid is filtered, strongly concentrated, and redissolved in water; and one-fourth of the solution, after neutralisation with lead carbonate, is mixed with the remaining three-fourths. The solution filtered from the lead sulphate—which is free from lead—is then mixed with a strong solution of barium chloride, whereupon it deposits, together with a little barium sulphate, crystalline barium dinitrotolueneparasulphonate, which may be purified by recrystallisation from hot water. The average yield of this salt is 330 grams.

The acid separated from this salt by sulphuric acid, crystallises in pale-yellow rhombic prisms, $C^7H^5(NO_2)_2SO_3H + 2H_2O$, which soon change to a sandy powder; when very slowly separated, however, it does not exhibit this latter character; it acquires a sulphur-yellow colour in sunshine, and slowly becomes moist on exposure to the air. Its taste is very sour and bitter. It begins to soften at 110° , gives off its water of crystallisation at 140° , and melts at 165° . It is very soluble in water, alcohol, and ether. Its salts are for the most part but slightly soluble, become yellow to brownish on exposure to the air, and detonate sharply when heated.

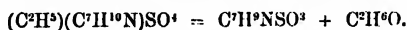
The *potassium salt*, $C^7H^5(NO_2)_2SO_3K$, obtained by decomposing the barium salt with potassium carbonate, crystallises from water in long white rhombic prisms; from alcohol in small, shining, strongly refractive plates. It dissolves in 191 pts. water at 14.5° , in 1190 pts. 94 per cent. alcohol at 22° , more freely in the same liquids at their boiling points, but is insoluble in ether. The *ammonium salt*, $C^7H^5(NO_2)_2SO_3NH_4$, obtained by neutralisation, forms white, flexible, rhombic prisms soluble in 24 pts. water at 18° . The *barium salt*, $[C^7H^5(NO_2)_2SO_3]^2Ba + 4H_2O$, crystallises in white silky prisms, which have a very bitter taste, and do not give off their water completely below 160° . The *calcium salt*, $[C^7H^5(NO_2)_2SO_3]^2Ca + 2H_2O$, forms groups of white needles and scales. The *lead salt*, obtained by neutralising the acid with lead carbonate, crystallises from hot aqueous solution in warty groups of yellowish needles containing $[C^7H^5(NO_2)_2SO_3]^2Pb + 2H_2O$; from the concentrated mother-liquor in yellow laminae with 3 mols. H_2O . The *copper salt*, $[C^7H^5(NO_2)_2SO_3]^2 + 4H_2O$, forms blue-green oblique rhombic prisms which give off their water at 160° .

The *chloride*, $C^7H^5(NO_2)_2SO_2Cl$, is prepared by heating the potassium salt with phosphorous pentachloride in a sealed tube at 150° for several hours, washing the viscid product with hot water, pressing and drying the residue, and exhausting the residue with boiling ether. It crystallises from ether in slender needles or long rhombic prisms, which melt at 123° – 125° , and dissolve also in alcohol.

The *amide*, $C^7H^5(NO_2)_2SO_2NH_2$, prepared by the action of ammonia on the chloride, and purified by recrystallisation from hot ammoniacal water with the aid of animal charcoal, forms white laminar crystals resembling those of benzoic acid; from alcohol it crystallises in rhombic needles. It is slightly soluble in hot water, becomes coloured when dried in the air, and melts at 203° .

Amidotoluenesulphonic Acids, or Toluidinesulphonic Acids, $C^7H^4NSO_3 = C^7H^4(CH_3)(NH_2)(SO_3H)$.

(1). **Orthotoluidene-metasulphonic Acid**, most probably $CH_3 : NH_2 : SO_3H = 1 : 2 : 5$. This acid is obtained: α . Together with a small quantity of a more soluble isomeride, by heating orthotoluidine with twice its weight of fuming sulphuric acid at 160° – 180° (Gerver, *Liebig's Annalen*, clxix. 373). β . By the action of heat on ethylsulphate of orthotoluidine (Pagel, *Ber.* vii. 1392):



γ . By the action of heat on orthotoluidine sulphate (Neville & Winther, *Chem. Soc. J.* 1880. xxxvii. 625):



δ . By the action of ammonium sulphide on the orthonitrotoluene-metasulphonic acid produced by the action of boiling alcohol under pressure on *o*-nitrodiazotoluene-m-sulphonic acid (Neville & Winther).

This sulphonic acid crystallises from water in yellowish oblique rhombic prisms or plates, $C^7H^4NSO_3H + 2H_2O$, which lose their water at 120° and crumble to a yellowish-white powder. It is readily soluble in hot water, but does not dissolve in absolute alcohol, ether, benzene, or chloroform. Its *potassium salt*, $C^7H^4NSO_3K + \frac{1}{2}H_2O$, is readily soluble in water and dilute alcohol, and forms silky crystals. The *sodium salt*, $C^7H^4NSO_3Na + H_2O$, forms feathery crystals, and dissolves freely in water, more sparingly in dilute alcohol. The *barium salt*, $(C^7H^4NSO_3)^2Ba + 3H_2O$, is readily soluble in water, sparingly in boiling dilute alcohol, and crystallises in long striated

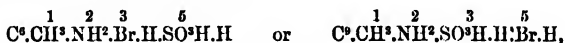
six-sided prisms. The *lead salt*, $(C^7H^5NSO_3)^2Pb + 1\frac{1}{2}H_2O$, crystallises from dilute alcohol in compact, white, six-sided prisms. The *silver salt*, $C^7H^5NSO_3Ag$, is a white precipitate consisting of small plates. When boiled with water it dissolves with partial decomposition, which however may be prevented by adding a few drops of nitric acid, and crystallises on cooling in white plates.

Orthotoluidinesulphonic acid dissolves in sulphuric acid, and on heating this solution strongly, sulphur dioxide is given off. When the acid is distilled with potash, orthotoluidine passes over, and the residue contains sulphuric acid and only a trace of sulphurous acid. On adding bromine in small quantity or in excess to the aqueous solution, *tribromorthotoluidine* (m. p. 112) is precipitated, and the solution contains dibromorthotoluidine-sulphonic acid, hydrobromic acid, and sulphuric acid (Gerver). According to Neville a. Winther, on the other hand, bromine slowly added to the aqueous acid in quantity not exceeding the molecular proportion, forms no precipitate but only a slight reddish opalescence; and if the liquid be then boiled, filtered, and evaporated, a *monobromotoluidinesulphonic acid*, $C^7H^4(NH^2)BrSO_3H$, crystallises out; and on further addition of bromine, a copious flocculent precipitate is formed, which, after purification by two or three distillations in a current of steam, crystallises from ether in long white needles, melting at $43-45^\circ$, and identical in every respect with the dibromorthotoluidine, $C^6CH^3.NH^2.Br.H.Br.H$, already mentioned (p. 1889).

From the constitution of this dibromotoluidine it may be inferred that the sulpho-group in the toluidinesulphonic acid from which it was formed, must occupy one of the meta-positions, 3 or 5 with regard to the CH^3 , and this conclusion is confirmed by the melting points of the sulphochloride and sulphonamide obtained from the toluene-sulphonic and bromotoluenesulphonic acids produced from this acid. On passing nitrous gas into a cold solution of the toluidinesulphonic acid, a tolylene-diazine sulphite, $C^7H^5N^2SO_3 = C^7H^5 \begin{smallmatrix} N=N \\ SO_3 \end{smallmatrix}$, is precipitated as a white slightly explosive

powder, which when heated on a water-bath with concentrated hydrobromic acid, is decomposed, with formation of a bromotoluenesulphonic acid; the potassium salt of which, when treated with phosphorus pentachloride, is converted into a sulphochloride, $C^7H^5(NH^2)SO_2Cl$, melting at $55.6-56.6^\circ$, agreeing therefore nearly with the bromotoluenesulphochloride (m. p. $52-53^\circ$), described by Hübner a. Müller (*Zeitschr. f. Chem.* 1870, 449) as having the sulpho-group in the meta-position relatively to CH^3 . The chloride heated with ammonia gives an amide melting at $146.2-147.2^\circ$. The toluenesulphonic acid obtained by heating the above-mentioned orthotolylene-diazine sulphite under pressure with alcohol, or by reducing the bromotoluenesulphonic acid with sodium-amalgam, gave, on treating its potassium salt with PCl_5 , a liquid sulphochloride which yielded with ammonia an amide melting at $106.5-107.5^\circ$ (Neville a. Winther), at 104° (Pagel).

To ascertain whether the sulpho-group is ortho- or para- to the amido-group, meta-bromorthotoluidine-metasulphonic acid,



was heated in a sealed tube with hydrochloric acid and water for several hours with the view of removing the sulpho-group, and leaving a monobromorthotoluidine; but instead of this a mixture was obtained consisting of a dibromorthotoluidine melting at $43-44^\circ$, and two monobromorthotoluidines, one an oil, the other a solid body melting at $54-57^\circ$ (ordinary bromotoluidine), whence it appeared that whichever of the two monobromotoluidines was first formed, was partly decomposed into dibromotoluidine and toluidine, and partly converted into an isomeric monobromotoluidine. To discover which of the two monobromotoluidines was formed in the first instance, ordinary monobromorthotoluidine, which is known to have the structure $C^6CH^3.NH^2.H.H.Br.H$, was heated with water or hydrochloric acid at 170° , or above, for many hours, but without undergoing any alteration. This seemed to show that the liquid bromotoluidine, $C^6CH^3.NH^2.Br.H^2$, must be the immediate product of the removal of the sulphur-group from the metabromorthotoluidine-metasulphonic acid. But to obtain further evidence of this, an attempt was made to prepare the bromotoluidine, $C^6CH^3.NH^2.Br.H^2$, by another process. For this purpose metabromometacetoluide, $C^6CH^3.H.Br.H.NH(C^2H^3O).H$, was nitrated with a mixture of 2 vol. nitric acid of sp. gr. 1.52, and 1 vol. of sp. gr. 1.45, and the acetyl-group was removed from the resulting nitro-compound by dissolving it in a freshly-made mixture of 2 vol. sulphuric acid and 1 vol. water. In this manner a base was obtained melting at $87-88^\circ$, and having the structure of *m*-brom-*o*-nitro-*m*-toluidine, $C^6CH^3.NO_2.Br.H.NH^2.H$, the NO_2 -group taking the para-position with respect to the NH^2 , according to a law previously established (p. 1887). This nitrobromotoluidine treated with a solution of nitrous gas in alcohol was converted into metabromortho

nitrotoluene, $C^6H^5.CH^3.NO^2.Br.H^2$, which distilled with steam as an oil, and gave, on reduction with tin and hydrochloric acid, liquid monobromotoluidine, $C^6H^5.NH^2.Br.H.H.H$. Lastly, on heating this compound with hydrochloric acid in a tube at 160° for twelve hours, and distilling the contents with steam, a substance was obtained which melted at $40^\circ-47^\circ$; and on neutralising the residue in the flask, and continuing the distillation, an oil was obtained, together with crystals melting at $53-56^\circ$ (ordinary monobromorthotoluidine melts at $55-56^\circ$). Hence it appears that the bromotoluidine which is the immediate product of the decomposition of metabromorthotoluidine-metasulphonic acid must have the constitution $C^6H^5.CH^3.NH^2.Br.H.H.H$; consequently the acid just mentioned must be represented by the formula $C^6H^5.CH^3.NH^2.Br.H.SO^3H.H$, and the corresponding orthotoluidine-metasulphonic acid by the formula $C^6H^5.CH^3.NH^2.H.H.SO^3H.H$, or $CH^3 : NH^2 : SO^3H = 1 : 2 : 5$ (Neville and Winther).

Orthotoluidine-parasulphonic Acid, $C^6H^5.CH^3.NH^2.H.SO^3H.H^2$, is obtained, together with paratoluidine-orthosulphonic acid, by the following process: A number of litre-flasks are charged with 200 c.c. toluene and 200 c.c. fuming sulphuric acid, and shaken, at first gently, afterwards more briskly, to make the liquids mix. To the viscid or crystalline mixture of ortho- and paratoluenesulphonic acid thus produced, nitric acid of sp. gr. 1.5 is added by drops, the liquids being strongly shaken after each addition, and then left to cool, and this treatment is repeated till the addition of a further quantity of nitric acid no longer produces any rise of temperature. The mixture of orthonitrotoluene-parasulphonic and paranitrotoluene-orthosulphonic acids is then poured into a sixfold volume of water, and the mixture, strained from any dinitrotoluene that may have separated, is neutralised with calcium hydrate. The acids are separated by means of their barium salts, or better of their lead salts (the salt of the orthonitro-acid in either case separating out first), and then converted into amido-acids by means of ammonium sulphide. If the nitro-acids have been separated by means of their calcium salts, the amido-acids formed from them require a further purification by conversion into barium salts, that of the orthamido-acid crystallising out first, while that of the paramido-acid remains in the mother-liquor (Weckwarth, *Liebig's Annalen*, clxxii. 191; *Ber.* vii. 450).

Orthotoluidine-parasulphonic acid crystallises in needles and prisms (Weckwarth). 100 pts. of water at 11° dissolve 0.974 parts of it; hot water dissolves it much more abundantly (Hayduck, *ibid.* clxxii. 204, and clxxiv. 343; *Ber.* vii. 552 and 1353). Its warm aqueous solution is coloured dark violet by ferric chloride. On adding a few drops of fuming nitric acid to the concentrated aqueous solution and diluting with water, a precipitate is formed, and if the liquid be then boiled it turns yellow (Weckwarth). The *barium salt*, $[C^6H^5(NH^2)SO^3]^2Ba + 24H^2O$, forms beautiful crystalline plates, which give off their water over sulphuric acid, dissolve easily in boiling, less easily in cold water. The *lead salt*, $[C^6H^5(NH^2)SO^3]^2Pb$, forms yellowish prisms, much less soluble than the barium salt (Hayduck).

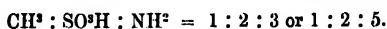
The acid is not altered by heating at 200° with fuming hydrochloric acid, or, with the exception of slight carbonisation, with fuming sulphuric acid, in which respect it differs from the paratoluidinesulphonic acids (p. 2018). When distilled with *potash* it gives off a large quantity of ammonia and a small quantity of aniline; by fusion with potash at a moderate heat it yields *o*-amidobenzoic (anthranilic) acid. It is not altered by fusion with sodium formate. Distilled with *manganese dioxide* and *sulphuric acid* it yields a distillate smelling of quinone, from which however only very small quantities of microscopic tablets can be obtained. By the action of *potassium chlorate* and *hydrochloric acid* it is converted into trichlorotoluquinone, $C^6H^3Cl^3O^2$, which crystallises in large, shining, yellowish plates, melting at 232° (p. 2029).

Orthotoluidine-parasulphonic acid is converted by bromine into dibromorthotoluidine-*p*-sulphonic acid, $C^6H^3Br^2(NH^2)SO^3H$, which crystallises from hot water in needles containing 1 mol. H^2O (p. 2021); by nitrous acid and alcohol into a diazin-compound, $C^6H^5\langle\frac{SO^3}{N=N}\rangle$, which forms a crystalline powder exploding when struck, and by cold fuming nitric acid into a nitrodiazin-compound, $C^6H^5(NO^2)\langle\frac{SO^3}{N=N}\rangle$, which separates on dilution with ice-cold water as a bulky white precipitate exploding by heat and by percussion.

Metatoluidine-orthosulphonic Acid, $C^6H^5.CH^3.H.NH^2.H.H.SO^3H$ (Lorenz, *Liebig's Annalen*, clxxii. 135; *Ber.* vii. 449). This acid is produced, together with a disulphonic acid, by heating 1 pt. metatoluidine with 3 pts. fuming sulphuric acid at $160^\circ-175^\circ$; on diluting the product with water, the monosulphonic acid is precipitated, while the disulphonic acid remains in solution.

Metatoluidine-orthosulphonic acid crystallises in thick rhombic plates, which dissolve sparingly in water, are insoluble in alcohol, and carbonise without previous fusion when heated above 275°. The barium salt, $(C^6H^4NSO_3)^2Ba + 9H_2O$, crystallises in thin plates or long prisms easily soluble in water. The lead salt, $(C^6H^4NSO_3)^2Pb + 3\frac{1}{2}H_2O$, forms crystalline nodules.

Bromine, added in excess to an aqueous solution of the acid, decomposes it completely into sulphuric acid, hydrogen bromide, and a tribromotoluidine, $C^6H^3Br_3.CH_3$, which crystallises from alcohol in reddish needles melting at 95° (p. 1998). On treating the toluidine-sulphonic acid immersed in alcohol of 60 per cent. with nitrous acid, it is converted into a diazo-acid, which when boiled with alcohol yields toluene-orthosulphonic acid. This shows that the amido-acid is a metatoluidine-orthosulphonic acid,



Lorenz represents it by the first of these formulæ; in other words, he regards it as a consecutive modification; but since the experiments of Neville a. Winther have shown that SO^3H , like Br , NO^2 , &c., when directly introduced into an amido-compound, takes by preference the para-position with respect to the NH^2 -group, it is more probable that the acid in question has the unsymmetrical constitution 1 : 2 : 5.

The metatoluidine-disulphonic acid, formed as above mentioned, decomposes very readily on evaporation into the monosulphonic acid and free sulphuric acid. Treated with baryta-water and carbon dioxide, it yields an acid barium salt, $(C^6H^4N.SO^3H.SO^3H)^2Ba + 12\frac{1}{2}H_2O$, crystallising in felted groups of slender needles, which give off their water at 160°. The lead salt, $C^6H^4N(SO^3H)^2Pb + 2H_2O$, forms hard yellowish-white crusts, sparingly soluble in water, insoluble in alcohol.

Paratoluidine-orthosulphonic Acid, $C^6H^4.CH^3.SO^3H.H.NH^2.H^2$ (Jenssen, *Lieb's Annalen*, clxxii. 230; *Ber.* vii. 55). This acid, identical with the toluidine-sulphonic acid described by Ruff and by Malyschew (vi. 283; vii. 1179), is formed, together with the *p-m*-modification, by the action of sulphuric acid on paratoluidine, and by reduction of paranitrotoluene-orthosulphonic acid (p. 2014) with hydrogen sulphide. It crystallises in hard colourless rhombohedrons, slightly soluble in hot water, insoluble in alcohol and ether. Its warm aqueous solution is coloured red by ferric chloride. On dissolving it in a few drops of fuming nitric acid, the liquid remains clear on dilution with water, and becomes blood-red on boiling. These characters distinguish it from the *o-p*-acid (Weekwarth, p. 2017). Bromine added to its boiling aqueous solution forms a bromamidodisulphonic acid, $C^6H^3Br(NH^2)SO^3H$ (p. 2020), convertible into a diazin-compound which crystallises in small yellow or brown needles, and may be transformed by the usual methods into the corresponding toluene-, cresol-, bromotoluene-, and chlorotoluene-sulphonic acids. The *toluene-sulphonic acid* thus obtained is identical with the β -acid described by A. Wolkow (vii. 1168); the *brominated acid*, with the parabromotoluenesulphonic acid of Hübner a. Post (p. 2009); and the *chlorinated acid* with the β -parachlorotoluenesulphonic acid described by Hübner a. Majert (p. 2013). The *paracresolsulphonic acid*, on the other hand, $C^6H^4(OH)SO^3H + 5H_2O$, is different from that which Engelhardt a. Lutschinoff obtained by the action of sulphuric acid on paracresol (vi. 506).

Paratoluidine-metasulphonic Acid, $C^6H^4.CH^3.H.SO^3H.NH^2.H^2$ (H. v. Pechmann, *Lieb. Ann.* clxxiii. 195). This acid, first described by Sell (v. 527), is formed, together with paratoluidine-orthosulphonic and a paratoluidine-disulphonic acid, by heating paratoluidine with fuming sulphuric acid. The relative quantities of these acids obtained vary with the temperature, the metasulphonic acid being produced most abundantly at comparatively low, the ortho- and the di-sulphonic acid at higher temperatures. Direct experiment shows that each of the monosulphonic acids, when heated for twenty minutes at 180°–200° with twice its weight of sulphuric acid, is partly converted (the metasulphonic acid for the greater part) into the isomeric monosulphonic and the disulphonic acids. The separation of the metasulphonic from the orthosulphonic acid is facilitated by the greater solubility of the former in water and especially in alcohol. The separation may also be effected, through the medium of the lead salts, the metasulphonate being but sparingly soluble, the orthosulphonate very easily soluble, in water. The disulphonate remains in the mother-liquor of the two monosulphonates.

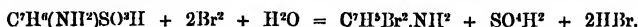
The paratoluidine-metasulphonic acid thus prepared agrees for the most part in its properties with that described by Sell, Malyschew, and Buff (vii. 1179). It dissolves at ordinary temperatures in 10 pts. water, is nearly insoluble in alcohol, and quite insoluble in ether. The crystals effloresce over sulphuric acid, and give off their water completely at 130°. The aqueous solution is coloured red by ferric chloride, especially when heated. The acid heated with water at -130° is resolved

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into sulphuric acid and toluidine, the latter being also formed on distilling the acid with potassium hydroxide. On fusing it with the latter, till the evolution of hydrogen slackens considerably, the chief product obtained is parahydroxybenzoic acid. It is not altered by fusion with sodium formate. The *barium salt*, $(C^7H^5NSO_3)^2Ba + 3H_2O$, crystallises from strong solutions in colourless six-sided laminae, easily soluble in water, insoluble in alcohol, and giving off their water at 130° . The *lead salt*, $(C^7H^5NSO_3)^2Pb + 2H_2O$, forms long colourless needles, much less soluble than the barium salt.

The corresponding diazin-compound, which is best prepared by treating the amido-acid with nitrous acid and alcohol under water at $30^\circ-40^\circ$, is converted by heating with alcohol under pressure into toluenemetasulphonic acid (p. 2018), by boiling with water into paracresolmetasulphonic acid (p. 2009), and by hydrobromic acid into parabromotoluene-metasulphonic acid (p. 2021).

Paratoluidine-metasulphonic acid, when added to cold fuming nitric acid, is converted into orthonitrodiazotoluene-metasulphonic acid, which, when boiled with alcohol under pressure, yields an *o*-nitrotoluene-*m*-sulphonic acid convertible by ammonium sulphide into *o*-toluidine-*m*-sulphonic acid (p. 2015). The *p*-toluidine-*m*-sulphonic acid, brought into contact with 2 mol. *bromine*, is completely resolved into sulphuric acid and dibromotoluidine:



With a larger quantity of bromine a similar reaction takes place, resulting in the formation of tribromotoluidine. When, however, bromine-vapour (1 mol.) is passed through a cold aqueous solution of the (*p-m*) acid, there is formed—together with a precipitate of dibromotoluidine—a bromoparatoluidine-metasulphonic acid (p. 2021), which remains in solution and may be separated therefrom by means of its sparingly soluble barium salt.

Bromamidotoluenesulphonic or Bromotoluidinesulphonic Acids, $C^7H^3Br(NH^2).CH_3$ M. Schäfer (*Liebig's Annalen*, clxxiv. 357; *Ber.* vii. 1355) has prepared the bromamido-acids analogous to Hübner a. Post's nitrobromotoluene-sulphonic acids (p. 2010) by reduction with ammonium sulphide; also the corresponding diazin-acids or tolyl-diazinsulphites by treating the amido-acids with nitrous gas and alcohol, and from these by boiling with water, the corresponding cresol-sulphonic acids. A comparative view of the properties of these several derivatives is given in the following table:

	Derivatives of nitro- <i>o</i> -bromotoluene- <i>m</i> -sulphonic acid	Derivatives of nitro- <i>p</i> -bromotoluene- <i>m</i> -sulphonic acid	Derivatives of nitro- <i>p</i> -bromotoluene- <i>o</i> -sulphonic acid
Free amido-acid	Crystallises hot from water in long rhombic laminae, from alcohol in nodules. Dissolves at 21° in 188 pts. water, and in 32 pts. alcohol. Resolved by bromine and water into sulphuric acid and tribromotoluidine, which crystallises from alcohol in yellow needles, and volatilises with steam in nearly white flocks melting at 82° .	Crystallises from water in grey-white needles. Very sparingly soluble in water, more freely in alcohol.	Crystallises from water in small well-defined prisms, sparingly soluble in water (1 pt. in 31), more freely in alcohol; yields with bromine and water a tribromotoluidine which crystallises from alcohol in yellow shining scales melting at 72° .
Barium salt	$[C^7H^3Br(NH^2)SO_3]^2Ba + H_2O$. Microscopic square plates, very soluble in water, sparingly in alcohol.	$[C^7H^3Br(NH^2)SO_3]^2Ba + 4H_2O$. Small, white nodules.	$[C^7H^3Br(NH^2)SO_3]^2Ba + 2H_2O$. White, easily soluble microscopic needles.

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	Derivatives of nitro- <i>o</i> -bromotoluene- <i>m</i> -sulphonic acid	Derivatives of nitro- <i>p</i> -bromotoluene- <i>m</i> -sulphonic acid	Derivatives of nitro- <i>p</i> -bromotoluene- <i>o</i> -sulphonic acid
Lead salt	$[C^7H^4Br(NH^2)SO^3]^2Pb + H^2O$. Easily soluble, elongated plates, turning yellow in the air.	—	—
Sodium salt	—	—	$C^7H^3(NH^2)SO^3Na + 2H^2O$. Indistinct, microscopic, very soluble crystals.
Diazin-compound	Brownish, easily decomposable powder, converted by water and by hydrobromic acid into <i>o</i> and the same cresolsulphonic acid.	Short, thick, red needles, exploding by percussion, and easily decomposed by water, alcohol, and hydrobromic acid.	Pale red microscopic (rhombic?) crystals, detonating when struck or when heated to 160°. Easily decomposable. Converted by HBr into dibrom- <i>o</i> -toluenesulphonic acid.
Cresolsulphonic acid	—	—	Brown syrup.
Barium salt	Prepared with water: greyish-white, indistinct, very soluble crystals, containing $4H^2O$. Prepared with HBr: Spicular crystals containing $3H^2O$.	$[C^7H^4Br(OH)SO^3]^2Ba + H^2O$. Easily soluble laminæ.	$[C^7H^4Br(OH)SO^3]^2Ba + 3H^2O$. Easily soluble, long white branched needles.
Lead salt	$[C^7H^4Br(OH)SO^3]^2Pb + 2H^2O$. Long white four-sided prisms, quickly turning yellow on exposure to the air.	—	—

Bromoparatoluidine-orthosulphonic acid, $C^7H^4Br(NH^2)SO^3H$, obtained by the action of bromine on a boiling aqueous solution of *p*-toluidine-*o*-sulphonic acid (p. 2018), crystallises in white, shining, slender needles, which become dark on exposure to light, and in solution; dissolve but very sparingly in water even at the boiling heat; are insoluble in alcohol and ether, but dissolve with moderate facility in hydrochloric and hydrobromic acid. It does not yield bromotoluidine when fused with potash. Its *potassium salt*, $C^7H^4BrNSO^3K + H^2O$, forms thick, hard, soluble prisms. The *barium salt*, $(C^7H^4BrNSO^3)^2Ba + 7H^2O$, crystallises from water in thick prisms, from alcohol in beautiful needles; gives off almost all its water of crystallization over sulphuric acid; dissolves easily in water, less easily in alcohol. *Lead salt*, easily soluble laminæ. *Silver salt*, white needles, which very easily turn brown, and are but slightly soluble in cold water (Jenssen, *Liebig's Annalen*, clxxii. 230; *Ber.* vii. 55). According to Weckwarth (*Ber.* vii. 450), this brominated acid, treated under alcohol with nitrous gas, is converted into a diazin-compound, $C^7H^4Br \begin{smallmatrix} SO^3 \\ \diagup \\ N=N \end{smallmatrix}$, which when heated with alcohol yields a bromotoluenesulphonic acid, apparently identical with Wroblewsky's β -acid (vii. 1172), and therefore consisting of meta-bromotoluene-orthosulphonic acid (p. 2012). Consequently the bromamido-acid

under consideration must be a metabromoparatoluidine-orthosulphonic acid, $C^6H^3SO^3H.Br.NH^2.H^2$ or $C^6H^3SO^3H.H.NH^2.Br.H$. This acid boiled with silver nitrate gives up the whole of its bromine as silver bromide. With fuming nitric acid it forms a red solution, which, when carefully diluted with a small quantity of water, deposits after some time shining yellow laminae of the diazin-nitro-compound, $C^7H^4(NO^2)Br<\overset{SO^3}{N=N}>$, which detonate when heated, and dissolve in water with evolution of nitrogen and formation of a nitrobromocresolsulphonic acid (Weckwarth).

Bromoparatoluidine-metasulphonic acid is formed, together with dibromotoluidine, on passing the vapour of bromine (1 mol.) through the cold aqueous solution of paratoluidine-metasulphonic acid (p. 2018), the dibromotoluidine being precipitated, while the brominated sulphonic acid remains in solution, and may be separated therefrom by means of its sparingly soluble barium salt. The free acid, $3C^7H^3Br(NH^2)SO^3H + 2H^2O$, crystallises from water or alcohol, in which it is readily soluble, in yellow needles, which give off their water of crystallisation at 130° , and decompose without previous fusion at a temperature above 200° . It is insoluble in ether. It is not altered by boiling with aqueous potash, but when distilled with potassium hydroxide it yields bromotoluidine as a colourless oil, which unites with acids forming crystallised salts.

Potassium Bromoparatoluidine-metasulphonate, $C^7H^3BrNSO^3K$, forms thick colourless prisms, moderately soluble in cold, more soluble in hot water. The *barium salt*, $(C^7H^3BrNSO^3)^2Ba + 2H^2O$, forms hard, shining, colourless plates, which do not effloresce over sulphuric acid; it dissolves sparingly in cold, more freely in hot water, but is insoluble in alcohol. The *lead salt*, $(C^7H^3BrNSO^3)^2Pb$, forms colourless shining needles, very slightly soluble in cold, more freely in hot water. The *silver salt*, $C^7H^3BrNSO^3Ag$, is precipitated by silver nitrate from the solution of the ammonium salt in thin short needles, and crystallises from hot water in long colourless needles. It is nearly insoluble in cold water, and turns grey when exposed to light.

The brominated amido-acid is converted by nitrous acid into a brown-red pulverulent diazin-compound, $C^7H^3Br<\overset{SO^3}{N=N}>$, which, when heated with alcohol under pressure, yields a bromotoluenemetasulphonic acid (p. 2013), (v. Pechmann, *Ber.* vii. 452).

Dibromorthotoluidine-parasulphonic acid, $C^7H^4Br^2(NH^2)SO^3H + H^2O$, produced by the action of bromine on orthotoluidine-parasulphonic acid (p. 2017), crystallises from hot water in long capillary needles; from hot alcohol in stellate groups of needles. Both these solvents dissolve it with difficulty in the cold, readily at boiling heat. At a higher temperature the acid gives off its crystallisation-water and crumbles to a hygroscopic powder, and at a still stronger heat (150°) it decomposes without previous fusion. The *barium salt*, $[C^7H^4Br^2(NH^2)SO^3]^2Ba + 9H^2O$, forms spherical groups of needles easily soluble in water, and becoming anhydrous over sulphuric acid. Cold fuming nitric acid converts it into a nitrodiazin-compound, which forms a white precipitate consisting of microscopic needles (Hayduck, *Ber.* vii. 1353).

Diamidotolueneparasulphonic or Tolylenediamineparasulphonic Acids, $C^7H^{10}N^2SO^3 = C^7H^2(NH^2)^2SO^3H.CH^3$ (H. Schwanert, *Liebig's Annalen*, clxxvi. 360) is formed by the action of ammonium sulphide on the corresponding dinitro-acid (p. 2014), and crystallises from hot water, in presence of animal charcoal, in white, striated, shining, translucent, oblique rhombic prisms, which turn grey when exposed to light, do not melt even at 280° , dissolve in 1470 pts. water at 14° , more freely in hot water, but are insoluble in alcohol. The aqueous solution quickly turns yellowish-brown. The solutions of its salts also quickly become dark-coloured when evaporated; they crystallise with difficulty or not at all, and are not precipitated by alcohol. The *barium salt*, $(C^7H^9N^2SO^3)^2Ba + 4H^2O$, is obtained, on evaporating its solution prepared with barium carbonate, as a blue-grey amorphous residue, which, after repeated solution and treatment with animal charcoal, becomes lighter in colour, but not quite white; it dissolves readily in water and in alcohol. A *lead salt* has been obtained, crystalline, but not of constant composition. The *potassium salt* is obtained by evaporation of its solution only as a brown uncrystallisable syrup.

With *acids*, on the other hand, the diamido-acid easily forms crystallisable compounds, which, however, must be recrystallised from acidulated water, since they are decomposed by pure water. The *hydrochloride*, $C^7H^{10}N^2SO^3.HCl + 2H^2O$, forms white to silver-grey, shining, short oblique rhombic prisms, soluble in water, slightly also in alcohol. The *hydrobromide* is analogous in composition, and exhibits similar characters. The *nitrate*, $C^7H^{10}N^2SO^3.NO^3H + H^2O$, forms a light felted faintly reddish mass, com-

posed of small oblique rhombic needles, soluble in water, slightly also in alcohol. The sulphate, $(C^6H^4N^2SO^3)^2SO^4H^2 + H^2O$, crystallises in white shining rhombic laminae.

Monobromodiamidotoluene-parasulphonic acid, $C^6HBr(NH^2)^2(SO^3H).CH^3$, is formed by drenching the diamido-acid with 20 pts. hot water, and adding bromine by drops (1 mol. bromine to 2 mol. of the acid), and crystallises from the resulting green-blue solution on cooling in small greyish-green shining tablets, or short thick rhombic prisms, with unequal pyramidal end-faces, sparingly soluble in water. The *potassium salt*, $C^6H^2BrN^2SO^3K + 2\frac{1}{2}H^2O$, is obtained by evaporating its brownish-yellow solution, taking care that no solid salt separates out on the edges, in geodes of pale-yellow tablets, very easily soluble in water, nearly insoluble in alcohol. When heated to 100° , it gives off its water, but does not change colour; but when quickly heated to 105° , or dehydrated at 120° , it turns blue, without loss of weight, and then dissolves in water with splendid blue colour. The yellowish salt cannot be recovered from the blue solution, which, when evaporated, leaves a blue amorphous salt (hence the precaution above mentioned). The *barium salt* is a greyish-white crystalline substance, containing a wrying amount of barium, very soluble in water, and turning blue under the same circumstances as the potassium salt; the free acid likewise exhibits a similar behaviour.

When 1 mol. *bromine* is added by drops to 1 mol. of the diamido-acid under 20 pts. hot water, a greyish-green crystalline powder separates, which may be regarded as a mixture of the mono- and dibrominated acids, and when heated at 120° with hydrobromic acid and amorphous phosphorus, is reconverted into the diamidotoluene-sulphonic acid. Larger quantities of bromine produce more complete decomposition.

The diamido-acid treated with *nitrous acid* and alcohol is converted into a brown-red amorphous diazin-compound which has not been exactly investigated.

Hydroxytoluenesulphonic or Cresolsulphonic Acids, $C^6H^3(CH^3)OH.SO^3H$, are formed by heating the corresponding tolyl-diazin sulphites, $C^6H^3\langle\begin{smallmatrix} SO^3 \\ N=N \end{smallmatrix}\rangle$ (so-called diazotoluenesulphonic acids) with water (vii. 932, 934), and by heating cresols with sulphuric acid (vi. 506; vii. 932, 934; viii. 583).

Orthocresol-parasulphonic acid, $C^6.CH^3.OH.H.SO^3H.H^2$, which Engelhardt a. Latschinoff obtained by heating *o*-cresol with sulphuric acid (vi. 507), may also be prepared by boiling the diazin-derivative of *o*-toluidine-*p*-sulphonic acid with water, or adding it to fuming sulphuric acid. It forms a *barium salt*, $[C^6H^3(OH)SO^3]^2Ba + 1\frac{1}{2}H^2O$, which crystallises in granular masses of microscopic prisms. The *potassium salt*, $C^6H^3(OH).SO^3K + \frac{1}{2}H^2O$, separates from boiling absolute alcohol as a yellowish crystalline powder, from aqueous alcohol in tufts of short needles. The acid fused with potash is converted into salicylic acid (Hayduck, *Ber.* vii. 552).

A cresolsulphonic acid, apparently identical with the above, is obtained as a potassium salt by fusing potassium toluenedisulphonate (p. 2009) with potassium hydroxide at 190° – 205° . The solution of the melt is acidulated with sulphuric acid; freed by means of ether from small quantities of salicylic acid; neutralised with potassium carbonate; freed from potassium sulphate by crystallisation; again acidulated to a pasty consistence; and mixed with ether-alcohol to complete the precipitation of the potassium sulphate. For further precipitation, the acid is converted into the barium salt, which crystallises with great facility, and separated therefrom by sulphuric acid.

The free sulphonic acid crystallises in feathery groups which retain $\frac{1}{2}$ mol. water at 100° ; it melts at 80° – 81° , and turns brown when heated above 100° ; it is hygroscopic, dissolves readily in alcohol and ether, and its aqueous solution gives with ferric chloride a coloration which disappears on addition of mineral acids or of alcohol. The *potassium salt*, $C^6H^3(OH)SO^3K + 2H^2O$, crystallises in well-defined prisms which dissolve readily in hot alcohol, swell up at 120° , melt without decomposition at 225° – 230° , and are decomposed by melting potash at 260° – 270° . The *sodium salt* forms plates or tablets containing 2 mol. H^2O . The *ammonium* and *cadmium salts* crystallise in prisms or needles. The *barium salt*, $[C^6H^3(CH^3)(OH)SO^3]^2Ba + H^2O$, crystallises readily in small prisms, insoluble in alcohol, and becoming anhydrous at 170° . The aqueous solution forms no precipitate with baryta-water, but is coloured blue by ferric chloride. The *calcium salt*, $(C^6H^3O^4S)^2Ca + 1\frac{1}{2}H^2O$, crystallises in stellate groups of needles which become anhydrous at 100° . The *lead salt*, $(C^6H^3O^4S)^2Pb + 3H^2O$, is readily soluble in water and in hot alcohol, and crystallises in silky needles, which give off their water at 160° . The *copper salt*, $(C^6H^3O^4S)^2Ca + 8H^2O$, crystallises in large square tablets; the *silver salt* in concentric groups of anhydrous needles, which are sensitive to light; the *zinc salt* in larger prisms, containing $10\frac{1}{2}$ mol. water, of which they lose $8\frac{1}{2}$ at 100° , the other 2 at 190° (C. Bruner, *Wien. Akad. Ber.* [2 Abth.], lxxviii. 665).

E. Baumann (*Ber.* xi. 1907) describes the potassium salt of an orthocresolsulphonic acid obtained by heating *o*-cresol with potassium hydroxide and water, leaving the solution to cool to 60°–70°, and digesting it at that temperature with potassium pyrosulphate. It crystallises in shining laminae, somewhat more soluble in water and in alcohol than potassium paracresolsulphonate.

Potassium cresolsulphonate (a mixture of several modifications) occurs, together with the phenolsulphonate, in horse-urine. It is somewhat less soluble than the latter in water and in alcohol; reacts similarly with water, acids, and alkalis, but decomposes somewhat more quickly on keeping, and is gradually decomposed during the putrefaction of the urine. The dry potassium salts of the cresolsulphonic acids are converted at 140°–150° into sulphonic acids which give a deep blue coloration with ferric chloride (Baumann).

TOLUIC ACIDS, $C^6H^4O^2 = C^6H^4(CH^3).COOH$. The ethylic ether of *orthotoluic acid* is formed by the action of ethyl chlorocarbonate on ortho-iodotoluene (p. 1994). The acid separated from the ether thus obtained melts at 102.5°.

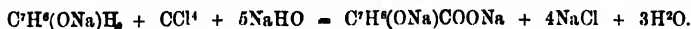
Orthotoluic acid in alkaline solution, heated with potassium permanganate, is oxidised to orthophthalic acid, $C^6H^4O^4$ (Weith, *Ber.* vii. 1057).

Bromoparatoluic Acid, $C^6H^3Br(CH^3).COOH$, is prepared by dropping bromoparaxylene into a solution of 5 to 10 g. chromic acid in 100 g. glacial acetic acid; heating the liquid on the water-bath for an hour; precipitating with water; distilling off the undecomposed bromoxylene with steam; and washing the precipitate with water. The acid thus produced appears to be identical with that which Landolph obtained from bromocymene (vii. 1175). It is easily soluble in alcohol and ether, insoluble in cold water, slightly soluble in boiling water, and crystallises therefrom in small shining needles melt. at 203.5°–204°; sublimes in shining elongated laminae. Its *barium salt*, $(C^6H^3BrO^2)^2Ba + 4H^2O$, crystallises in concentric groups of short capillary needles, very slightly soluble in cold, much more freely in hot water. The *calcium salt*, $(C^6H^3BrO^2)^2Ca + 3H^2O$, is somewhat more soluble, and crystallises in arborescent groups of short hard needles (Januassch u. Dieckmann, *Liebigs Annalen*, clxxi. 83).

Nitrotoluic Acids. Fittica (*Liebigs Annalen*, clxxi. 303; *Ber.* vi. 938; vii. 1357, 1529) distinguishes three mononitrotoluic acids, $C^6H^3(NO^2)O^2$, viz.: α . Produced by dropping cymene into red fuming nitric acid of sp. gr. 1.5. Kept in a state of gentle ebullition, this acid melts at 189°.— β and γ . Formed by oxidising liquid and solid nitrocymene (p. 622) respectively with chromic acid. These two acids resemble one another in subliming without previous fusion, in forming very similar salts, and in giving with lead, mercury, and silver salts white precipitates insoluble in alcohol. The γ -acid differs, however, from the β -acid in being very nearly insoluble in water whether cold or hot, and only slightly soluble in alcohol of 90 per cent. Moreover, the alcoholic solution of the β -acid remains clear when mixed with solution of platinic chloride, whereas that of the γ -acid gives after some time a yellow crystalline precipitate. Both acids are scarcely attacked by tin or zinc and hydrochloric acid, but sodium-amalgam converts them into the corresponding diazin-toluic acids.

Diazin-toluic Acids, $C^6H^4N^2O^4 = CO^2H.C^6H^3.N = N.C^6H^4.CO^2H$. The nitro-acid in alkaline solution is left in contact with the sodium-amalgam for about a day, till the addition of acetic acid in excess no longer produces a precipitate, and the diazin-acid is then precipitated with hydrochloric acid, or extracted from the acetic solution by ether. The β -acid when recrystallised from boiling water forms yellowish microscopic needles, which melt at 182°–184°, dissolve readily in alcohol, ether, and acetic acid, with moderate facility in boiling water, scarcely at all in cold water. The same diazin-acid is formed in like manner from a nitrotoluic acid. γ -*diazin-toluic acid*, when purified by recrystallisation from boiling alcohol, forms tufts of yellowish-brown needles nearly insoluble in water whether hot or cold, moderately soluble in boiling alcohol and in acetic acid, still more soluble in ether. It sublimes at about 240° without previous fusion, blackening at the same time (Fittica, *loc. cit.*)

Hydroxytoluic Acids, $C^6H^3(OH)(CH^3)(COOH)$. *Oxytoluic, Homohydroxybenzoic, or Cresotic acids*.—These acids are formed: 1. By the action of carbon dioxide on the sodium-cresols (p. 583). 2. By oxidation of the corresponding aldehydes, most readily by introducing the aldehydes into fused potash containing a little water, continuing the fusion for a few minutes, then adding water and precipitating with hydrochloric acid (Tiemann u. Schotten, *Ber.* xi. 767). 3. By the action of carbon tetrachloride on a strongly alkaline solution of a sodium-cresol:



By this reaction, orthocresol is converted into orthohomo-orthohydroxybenzoic or

orthohomosalicyclic and orthohomoparahydroxybenzoic acids.* As in other reactions in which ortho- and para-compounds are produced simultaneously, the ortho-compounds are formed most abundantly at high, and the para-compounds at low temperatures; and for this reason the carbon tetrachloride reaction is best adapted for preparing the homoparahydroxybenzoic acids, whereas the homo-orthohydroxybenzoic or homosalicyclic acids are better prepared by the action of carbon dioxide on the sodium-derivatives of the cresols: for as this reaction takes place at about 200°, these ortho-compounds are produced by it in much larger quantity than the para-compounds (E. Schall, *Ber.* xii. 816).

The following hydroxytoluic acids, obtained by oxidation of the corresponding aldehydes, are described by Tiemann & Schotten, *loc. cit.*

a. From Orthocresol:

Orthohomosalicyclic acid, [OH : CH³ : COOH = 1 : 2 : 6], melting at 159°–160°, is identical with β-cresotic acid (p. 584).

Orthohomoparahydroxybenzoic acid, 1 : 2 : 4, is sparingly soluble in cold water and chloroform, easily soluble in boiling water, alcohol, and ether, and crystallises from water in small faintly flesh-coloured needles containing $\frac{1}{3}$ mol. crystallisation-water, and melting at 172°–173°.

b. From Metacresol:

Metahomosalicyclic acid, 1 : 3 : 6, identical with γ-cresotic acid, melts at 173°.

Metahomoparahydroxybenzoic acid, 1 : 3 : 4, crystallises from water in small white needles containing $\frac{1}{4}$ mol. water, and melting at 177°–180°.

c. From Paracresol:

Parahomosalicyclic acid, [1 : 4 : 6], identical with α-cresotic acid, melts at 151°.

The homosalicyclic acids behave with solvents and reagents almost exactly like salicylic acid. They dissolve but sparingly in cold water, more readily in boiling water, easily in alcohol and chloroform. From water or weak spirit they crystallise in dazzling white needles, undistinguishable from crystals of salicylic acid. They also give the salicylic acid reaction with ferric chloride. In exactly neutralised solutions of the ammonium salts, barium chloride produces no precipitate, cupric sulphate a yellow-green crystalline precipitate of a neutral copper salt, soluble in a large quantity of hot water. In solutions containing excess of ammonia, basic compounds are formed in both cases. Silver nitrate produces in neutral solutions of the ammonium salts, white precipitates, very sparingly soluble in water, easily in ammonia; lead acetate, white precipitates easily soluble in acetic acid.

The homoparahydroxybenzoic acids are but sparingly soluble in cold water, still less in chloroform, but dissolve readily in hot water, alcohol, and ether. They do not give any characteristic colour-reactions with ferric chloride. The normal barium and calcium salts are easily soluble; the solutions treated with ammonia do not give precipitates of basic salts. In neutral solutions of the ammonium salts, cupric sulphate forms a blue-green precipitate very slightly soluble in water; but on adding cupric sulphate and a little ammonia to these same solutions, precipitates are formed consisting of basic salts which dissolve with blue colour in excess of ammonia. The silver and lead salts are white compounds sparingly soluble in water (Tiemann & Schotten).

There are four possible homologues of metahydroxybenzoic acid, but the corresponding aldehydes are not produced by the chloroform reaction. One of these hydroxytoluic acids, viz. orthohomometahydroxybenzoic acid, [1 : 2 : 5], is formed: (1). Together with hydroxyterephthalic acid, C⁶H³(OH)(CO²H)(CO²H), [1 : 2 : 5], by fusing sulphotoluic acid, C⁶H³(CH³)(SO³H)(CO²H), with potash. The two acids thus produced cannot easily be separated by crystallisation, but the separation may be effected by the application of a gentle heat, the hydroxytoluic acid then subliming alone (Flesch, *Ber.* vi. 481). (2). By passing nitrous gas into a nitric acid solution of the amidotoluic acid (m. p. 184°), which Ahrens obtained by reduction of one of the nitrotoluic acids resulting from the action of nitric acid on coal-tar xylene (vii. 1180).

This acid crystallises in long needles having a silky lustre, sparingly soluble in cold, easily in hot water, alcohol, and ether, insoluble in chloroform. It melts at 203°–204° (corr. 206°–207°), volatilises with vapour of water, and does not give any coloration with ferric chloride. Its lead salt crystallises with 2H₂O in needles having a diamond lustre. The calcium salt contains 4H₂O. The ethylic ether crystal-

* In the names of these hydroxytoluic acids, the positions of the side-chains are referred to the phenolic hydroxyl which stands in the position 1; the first prefix, ortho, &c. (standing before 'homo') refers to the CH³-group, and indicates the cresol from which the acid is derived, while the second prefix, o-, m-, or p-, coming after 'homo,' indicates the position of the CO²H-group.

lises in wavelitic geodes, melts at 74°-75°, and solidifies at 60°-62°. The acid heated with methyl iodide and potassium hydroxide is converted into the *dimethylic ether*, $C^6H^2(CH^3)(OC^2H^5)(CO^2CH^3)$, and this latter boiled with potash yields methyl-hydroxytoluic acid, $C^6H^2(CH^3)^2(OH)(CO^2H)$, which crystallises in beautiful sublimable needles, melts at 156°, is insoluble in cold water, but dissolves readily in alcohol and in ether. Its *barium salt* contains $4H^2O$. Orthohomometahydroxybenzoic acid is not decomposed by hydrochloric acid, even at 270°, but its potassium-salt, heated with quicklime, yields a liquid cresol which boils at 185°-187°, and when fused with potash, yields nothing but salicylic acid (E. v. Gerichten a. W. Rössler, *Ber.* xi. 705, 1886).

Methoxytoluic Acids, $C^6H^{10}O^3 = C^6H^2(OCH^3)(CH^3)(COOH)$ (C. Schall, *Ber.* xii. 816). The methylic ethers of these acids are best prepared by the action of methyl iodide on the sodium salts of the hydroxytoluic acids, $C^6H^2(ONa)(CH^3)COONa$. Those of the three meth-homosalicylic acids, $OCH^3 : CH^3 : COOH = 1 : 2 : 6$, $1 : 3 : 6$, $1 : 4 : 6$, are oily liquids smelling like winter-green oil, and decomposing partially when boiled.

Methylic Methoxy-orthomethylparabenzoate, or *Methylic Orthomoanisate*, $OCH^3 : CH^3 : COOH = 1 : 2 : 4$, crystallises in small plates melting at 67°, sparingly soluble in hot water, easily in alcohol, ether, benzene, and chloroform.

Methylic Methoxy-metamethylparabenzoate, or *Metahomoanisate* [$1 : 3 : 4$], is a thick oil.

These ethers, which are all volatile in steam, are converted into the corresponding acids by heating with excess of alkali:

OCH^3	CH^3	$COOH$	
1	2	6	Feathery needles, m. p. 81°
1	3	6	Groups of needles or plates, m. p. 103°
1	4	6	Long thin needles, m. p. 67°
1	2	4	Minute silky needles, m. p. 192°
1	3	4	Needles, m. p. 176°

These methoxytoluic acids are converted by oxidation with potassium permanganate in alkaline solution into the corresponding methoxyphthalic acids, $C^6H^2(OCH^3)(COOH)(COOH)$, and this transformation determines their constitutional formulae, and therefore the constitution of the corresponding hydroxytoluic acids (p. 1531). The structure of these latter cannot well be determined by converting them into hydroxyphthalic acids by fusion with potash, as this process is apt to lead to transpositions in the side-chains; neither can the constitution of a hydroxytoluic acid be determined by direct oxidation with permanganate, as the benzene-nucleus is then attacked and not the CH^3 -group.

The following table exhibits the relations between the hydroxytoluic and methoxytoluic acids and the corresponding derivatives of phthalic acid:

1.	2.	3.
Orthohomosalicylic acid, $C^6H^2.OH.CH^3.CO^2OH$ m. p. = 164°.	Metahomosalicylic acid, $C^6H^2.OH.CH^3.CO^2OH$ m. p. = 173°.	Orthohomomet-hydroxybenzoic acid, $C^6H^2.OH.CH^3.CO^2OH$ m. p. = 204°.
Methorthohomosalicylic acid, $C^6H^2.OCH^3.CH^3.CO^2OH$ m. p. = 81°.	Meth-metahomosalicylic acid, $C^6H^2.OCH^3.CH^3.CO^2OH$ m. p. = 103°.	Methoxyortho-methylmetabenzoic acid, $C^6H^2.OCH^3.CH^3.CO^2OH$ m. p. = 156°.
β-Methoxyisophthalic acid, $C^6H^2.OCH^3.CO^2OH.CO^2OH$ m. p. = 217°.	Methoxyterephthalic acid, $CH^3.OCH^3.CO^2OH.CO^2OH$ m. p. = 278°.	
β-Hydroxyisophthalic acid, $C^6H^2.OH.CO^2OH.CO^2OH$ m. p. = 239°.	Hydroxyterephthalic acid, $C^6H^2.OH.CO^2OH.CO^2OH$ m. p. above 300°.	

4.	5.	6.
Parahomosalicylic acid, $\text{C}^6\text{H}^1.\text{OH}.\text{CH}^4.\text{COOH}^6$ m. p. = 151°.	Orthohomoparahydroxy- benzoic acid, $\text{C}^6\text{H}^1.\text{OH}.\text{CH}^2.\text{COOH}^4$ m. p. = 172°.	Metahomoparahydroxy- benzoic acid, $\text{C}^6\text{H}^1.\text{OH}.\text{CH}^3.\text{COOH}^4$ m. p. = 178°.
Methparahomosalicylic acid, $\text{C}^6\text{H}^1.\text{OCH}^4.\text{CH}^6.\text{COOH}$ m. p. = 67°.	Methoxyorthomethyl- parabenzoic acid, $\text{C}^6\text{H}^1.\text{OCH}^2.\text{CH}^4.\text{COOH}$ m. p. = 192°.	Methoxymetamethylpara- benzoic acid, $\text{C}^6\text{H}^1.\text{OCH}^3.\text{CH}^4.\text{COOH}$ m. p. = 176°.
α -Methoxyisophthalic acid, $\text{C}^6\text{H}^1.\text{OCH}^1.\text{COOH}^2.\text{COOH}^4$ m. p. = 261°.		Methoxyorthophthalic acid, $\text{C}^6\text{H}^1.\text{OCH}^3.\text{COOH}^3.\text{COOH}^4$ m. p. = 138°-144°.
α -Hydroxyisophthalic acid, $\text{C}^6\text{H}^1.\text{OH}^2.\text{COOH}^4.\text{COOH}$ m. p. above 300°.		Hydroxyorthophthalic acid, $\text{C}^6\text{H}^1.\text{OH}^3.\text{COOH}^4.\text{COOH}$ m. p. = 181°.

Sulphotoluic Acid, $\text{C}^6\text{H}^4(\text{CH}^3)(\text{CO}^2\text{H})(\text{SO}^3\text{H})$. This acid is obtained by oxidation of thiocymene (from camphor) with nitric acid, and may be purified by conversion into the lead salt and decomposition of the latter with hydrogen sulphide, these operations being repeated several times. It crystallises from aqueous solution in long thin hydrated prisms (Flesch, *Ber.* vi. 481); in concentric groups of needles containing 1 mol. water, easily soluble in water, alcohol, and ether (Bechler, *J. pr. Chem.* [2], viii. 170). The *potassium salt*, $\text{C}^6\text{H}^4(\text{CO}^2\text{H})(\text{SO}^3\text{K}) + 3\text{H}^2\text{O}$, crystallises from a solution of the acid incompletely neutralised with potash, in well-defined prisms. The *lead salt*, $\text{C}^6\text{H}^4(\text{SO}^3)(\text{SO}^3)\text{Pb} + 3\text{H}^2\text{O}$, separates immediately as a granular powder on adding lead carbonate to the warm aqueous solution of the acid; by evaporating the solution it may be obtained in granular crusts (Flesch). According to Bechler (who, however, did not obtain it quite pure) it contains only 1 mol. H^2O . The *magnesium salt*, $\text{C}^6\text{H}^4(\text{CO}^2)(\text{SO}^3)\text{Mg} + 3\text{H}^2\text{O}$, crystallises in tufts of colourless needles, very easily soluble in water (Bechler).

By fusion with potash, this sulphotoluic acid is converted into a hydroxytoluic acid melting at 202°-203°, and therefore different from any of the five hydroxytoluic acids above described (Flesch).

Fittica (*Liebig's Annalen*, clxxii. 328; *Ber.* vi. 942) describes a sulphotoluic acid isomeric with the above, obtained by adding thiocymene from thymol to nitric acid of sp. gr. 1.2, and evaporating the solution to dryness on a water-bath, and purified by boiling the residue with alcohol, decanting the mother-liquor from the crystals which separate on cooling, and recrystallising the product several times. The acid thus prepared is insoluble in water, sparingly soluble in alcohol, and crystallises therefrom in stellate groups of anhydrous needles melting at 190°. It dissolves in ammonia; blackens, and yields sulphuric acid when boiled with aqueous potash, soda, or baryta; and is decomposed even by heating with water or calcined magnesia. Its *magnesium salt*, $\text{C}^6\text{H}^4(\text{CO}^2)(\text{SO}^3)\text{Mg}$, formed by boiling the alcoholic solution of the acid with magnesia, separates in yellowish crystals, which under the microscope exhibit rhombic forms.

Alphatoluic or Phenylacetic Acid, $\text{C}^6\text{H}^5.\text{CH}^2.\text{COOH}$. The amide of this acid is formed by prolonged heating of benzyl cyanide with an alcoholic solution of potassium hydrosulphide (p. 314), and when heated with alcoholic potash is converted into the acid melting at 66°-67°.

Potassium phenylacetate is decomposed by the electric current into the base and acid, but the acid is quickly oxidised by the oxygen and ozone evolved at the positive pole, to benzaldehyde and benzoic acid. A solution of the free acid is but slowly electrolysed, yielding the same products, together with two neutral substances, one melting at 90°-93°, the other at 115° (Slawik, *Ber.* vii. 1051). Phenylacetic acid in alkaline solution is oxidised by potassium permanganate to benzoic acid; and when

ozonised oxygen is passed into the same solution, benzaldehyde is given off, and benzylic phenylacetate, $C^6H^5.CH^2.COOCH^2(C^6H^5)$, is obtained as a light yellow liquid having a faint aromatic odour, a density of 1.101, and boiling at 317° – 319° (Slawik).

Phenylacetic acid, heated with phthalic anhydride and sodium acetate, is converted into benzylidene-diphthalyl, $C^6H^4.C^2O^2.CH.C^6H^5$ (p. 1620).

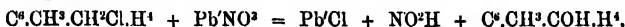
α-Tolunitril, Phenylacetoneitril, or Phenyl-methyl Cyanide, $C^6H^5.CH^2.CN$, is the chief constituent of the essential oils of the garden cress (*Lepidium sativum*) and the garden nasturtium (*Tropæolum majus*). See CRESS-OILS (p. 584).

Parabromalphatoluic acid, $C^6H^4Br.CH^2.COOH$, formed by heating *p*-bromobenzyl cyanide at 100° , with hydrochloric acid in sealed tubes, crystallises in long white needles, which melt at 114.5° . It decomposes carbonates very slowly, but dissolves readily in ammonia and soda-ley, forming salts. By oxidation with chromic acid it is converted into parabromobenzoic acid.

Ammonium parabromalphatoluate forms white needles easily soluble in water. The *silver salt*, $C^6H^4Br.CO^2Ag$, is a white precipitate nearly insoluble in water; the *copper salt*, $(C^6H^4Br.CO^2)^2Cu$, a bluish-green nearly insoluble precipitate; the *calcium and barium salts* crystallise from water in needles (Jackson a. Lowery, *Ber.* x. 1209).

Para-iodalphatoluic acid, $C^6H^4I.CH^2.COOH$, formed in like manner from the corresponding cyanide (p. 2007), and purified by crystallisation from boiling water, forms white acuminate plates melting at 135° , sublimes in needles, dissolves readily in hot water, also in alcohol, ether, benzene, carbon sulphide, and glacial acetic acid. By chromic acid mixture, it is oxidised to *p*-iodobenzoic acid. Its *silver salt*, $C^6H^4I.CH^2.COOAg$, crystallises from boiling water, in which it is slightly soluble, in shining plates; the *barium salt*, $(C^6H^4I.CH^2.COO)^2Ba + H^2O$, forms small white easily soluble needles; the *calcium salt*, easily soluble branching needles. With solutions of heavy metallic salts, *p*-iodalphatoluic acid forms variously coloured precipitates (Mabery a. Jackson, *Ber.* xi. 55).

TOLUIC ALDEHYDES, $C^6H^5O = C^6H^4(CH^3)COH$. *Orthotoluic Aldehyde* is prepared by heating orthoxylyl chloride, C^6H^4Cl , for an hour with $\frac{1}{2}$ mol. lead nitrate and 6 or 7 pts. water:



It is a yellowish, strongly refracting liquid, smelling like bitter almond oil and cinnamon oil, boiling at 200° , and forming a crystalline compound with hydrogen-sodium sulphite (Lauth a. Grimaux, *Bull. Soc. Chim.* [2], vii. 233; Rayman, *ibid.* xxvii. 498). By sodium-amalgam and water it is converted into the corresponding xylyl alcohol, $C^6H^4(CH^3).CH^2OH$, which crystallises in needles soluble in alcohol, slightly soluble in water, melts at 54° , and boils at 210° . At the same time there is formed a body analogous to hydrobenzoin, melting at 173° (Rayman).

Hydroxytoluic Aldehydes, $C^6H^5O^2 = C^6H^4(OH)(CH^3)COH$ (Tiemann a. Schotten, *Ber.* xi. 767). These compounds are prepared from the three isomeric cresols by the action of sodium hydroxide and chloroform:



20 pts. of the cresol are heated in a flask with inverted condenser with a solution of 50 pts. sodium hydroxide in 150 water, and 30 or 40 pts. of chloroform are gradually added. The mixture, which usually becomes cherry-red, is acidified at the conclusion of the reaction, and distilled in a current of steam. The aldehyde homologous with salicylic aldehyde then distils over, together with unaltered cresol. The remaining liquid, filtered from a resinous compound (rosolic acid), deposits on cooling crystals of a homologue of parahydroxybenzoic aldehyde, when ortho- or meta-cresol has been used; paracresol, on the other hand, does not yield a similar compound.

The homoparahydroxybenzaldehydes from *o*- and *m*-cresol, like parahydroxybenzaldehyde itself, form easily soluble compounds with hydrogen-sodium sulphite; the three homosalicilic aldehydes, on the other hand, like salicylic aldehyde itself, form sparingly soluble compounds with that salt.

Orthocresol, treated as above, yields the two following compounds:

Orthohomosalicilic aldehyde, $C^6H^4(OH)(CH^3)(COH) = (1 : 2 : 6)$, melting at 170° to an oil, which boils at 208° – 209° ; and

Orthohomoparahydroxybenzaldehyde, $C^6H^4(OH)(CH^3)(COH) = (1 : 2 : 4)$, crystallising from water in long feathery prisms, which melt at 115° .

From metacresol have been prepared:

Metahomosalicilic aldehyde, $C^6H^4(OH)(CH^3)(COH) = (1 : 3 : 6)$, melting at 54° , boiling at 222° – 223° ; and

Metahomoparaoxybenzaldehyde, $C^6H^3(OH)(CH^3)(COH) = (1 : 3 : 4)$, which crystallises from water in white tabular plates, which melt at 110° .

Paracresol gives only one aldehyde, namely :

Parahomosalicyclic aldehyde, $C^6H^3(OH)(CH^3)(COH) = (1 : 4 : 6)$, a bright yellow oil, solidifying at 40° . When crystallised from dilute alcohol, this aldehyde melts at 56° , and boils at 217° – 218° .

The three homosalicyclic aldehydes dissolve sparingly in water, easily in alcohol, ether, and chloroform. With ferric chloride, the ortho-aldehyde gives a bluish, the meta- a violet, and the para- a deep blue colour. They smell like salicylic aldehyde, which they further resemble in being coloured yellow by alkalis, and in the sparing solubility of their ammonium salts in excess of ammonia. Alcoholic solutions of these aldehydes, mixed with a little ammonia, give white precipitates with lead acetate and silver nitrate ; with copper sulphate they give green precipitates, which are not dissolved by excess of ammonia.

The two homoparahydroxybenzaldehydes dissolve in hot water, easily in alcohol, ether, and chloroform. With ferric chloride the ortho-compound gives a bluish violet, the meta-compound a bright rose-red colour. Their alkaline solutions are colourless. With metallic salts they behave like the homologues of salicylic aldehyde, but their precipitates with cupric sulphate dissolve in excess of ammonia.

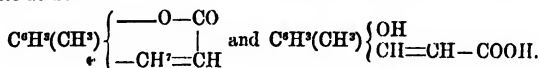
The hydroxytoluic aldehydes are converted by oxidation with potassium permanganate into the corresponding hydroxytoluic acids, very slowly when the aldehydes are simply dissolved in water, more readily in presence of acetic acid. The easiest way of effecting the conversion is to fuse the aldehydes with potassium hydroxide containing a little water, the fusion being continued for a few minutes, water then added, and the acids precipitated by hydrochloric acid (p. 2023).

Parahomosalicyclic aldehyde is remarkable for the facility with which it crystallises, and reacts with other bodies. By treating it, in quantities of a few grams, with excess of sodium-amalgam, for a day or two, neutralising *exactly* with sulphuric acid, and extracting with ether, *parahomosaligenin* (parahomosalicyclic alcohol), $C^6H^3(OH)(CH^3)(CH^2OH) = (1 : 4 : 6)$, is obtained in colourless brilliant needles, melting at 105° , which may be purified by crystallisation from a small quantity of hot water. Parahomosaligenin dissolves easily in alcohol and ether, and in all proportions in boiling water. It reacts like saligenin. In neutralising as above with sulphuric acid, a small quantity of a compound is usually precipitated, which melts at 200° – 205° , and probably consists of a homologue of saliretin.

When parahomosalicyclic aldehyde is boiled for five hours with methyl iodide and a solution of potash in methyl alcohol, and the mixture poured into water, *methyl-parahomosalicyclic aldehyde* separates as an oil, which, after washing with water and soda-solution, boils at 254° ; it smells like creasote, and does not react either with ferric chloride or with caustic soda.

The potassium derivative of the aldehyde, when suspended in anhydrous ether and treated with acetic anhydride, gives a corresponding *acetyl*-derivative, which melts at 57° , and is also unaffected by ferric chloride. It combines with hydrogen-sodium sulphite, and unites directly with 1 mol. of acetic anhydride, to form a compound from which the aldehyde character has entirely disappeared. This compound melts at 94° , and is completely decomposed by boiling water and by soda-solution.

An attempt was made, by boiling the aldehyde for an hour with an equal weight of dry sodic acetate and excess of acetic anhydride, to obtain homologues of coumarin and coumaric acid :



The product was poured into water, and the oil which separated taken up with ether. The ethereal solution was shaken, first with sodium-hydrogen sulphite solution to remove unaltered aldehyde, and then with sodium carbonate to remove acetocoumaric acid, which is always formed in this reaction. On evaporating the remaining ethereal solution, a well-crystallised product was obtained, which smelt of coumarin, and gave on analysis numbers which pointed to its being a mixture of methyl-coumarin and the above-mentioned addition-compound of acetoparahomosalicyclic aldehyde with acetic anhydride ; it melted between 60° and 88° . The acid extracted from the ethereal solution by sodium carbonate, having been boiled with alkalis to remove the acetyl-group, gave an acid which melted at 185° , and showed the crystalline form and reactions of orthocoumaric acid.

Parahomosalicyclic aldehyde and orthohomoparaoxybenzaldehyde, on nitration, yield only orthonitro-derivatives, the first melting at 141° , the second at 152° . Both are crystalline bodies, insoluble in cold, soluble in hot water, and both exhibit the

aldehyde character. Ordinary salicylic aldehyde, according to Mazzara, gives an ortho- and a para-nitro-derivative. But in the hydroxytoluic aldehydes above described, the para-position is already occupied, in the first by a methyl-group, in the second by a COH-group; these aldehydes, therefore, give only orthonitro-compounds (Schotten, *Ber.* xi. 784).

TOLUIDINES, $C^6H^4(NH^2).CH^3$. See **TOLUENES (AMIDO-)**, (pp. 1995, 2000)*.

TOLUQUINONE, $C^7H^4O^2 = C^6H^3(CH^3)O^2 = C^6.CH^3.O.H.H.O.H$ (Nietzky, *Ber.* x. 832, 1934). This compound is formed by the oxidation of paradiamidotoluene or of orthotoluidine dissolved in sulphuric acid, with manganese dioxide, potassium dichromate, or ferric salts; and in like manner, though less readily, from amidazotoluene. It crystallises in golden-yellow, sharply-pointed, rhombic laminæ, having the characteristic odour of quinones, very volatile, melting at 67°, slightly soluble in cold, more readily in hot water, very easily in alcohol and ether. The aqueous solution has a golden yellow colour, and is turned brown by alkalis.

Chlorotoluquinones. The di- and tri-chloro-derivatives of toluquinone, which Graebe and Borgmann obtained by the action of potassium chlorate and hydrochloric acid on the mixture of cresols from coal-tar, have been further examined by Southworth (*Liebig's Annalen*, clxviii. 267), who has prepared them from the pure isomeric cresols.

Metacresol treated with potassium chlorate and hydrochloric acid becomes first black, then red, and is ultimately converted into small yellow globules which quickly solidify and sink to the bottom; and by washing these with water and distilling them with steam, dichlorotoluquinone, $C^6H^2Cl^2O^2$, is obtained as a yellow crystalline mass. This compound crystallises from alcohol in yellow, transparent tables, which become brown on exposure to light. It is slightly soluble in water, but dissolves in alcohol and ether. It may be sublimed, but decomposes partially at the same time. Solution of sulphurous acid converts it very readily into the corresponding quinol, $C^6HCl^2.CH^3.(OH)^2$, a colourless body, which, when crystallised from water, retains water of crystallisation, probably $2H^2O$. It melts between 167° and 169°, and may be sublimed without decomposition. By treatment with acetyl chloride it furnishes an acetyl-derivative which crystallises from alcohol in small clustering needles melting between 122° and 124°.

Dichlorotoluquinone is not reduced to toluquinol by the action of sodium-amalgam.

Orthocresol similarly treated yields a mixture of di- and trichlorotoluquinone, convertible by reduction with sulphurous acid into the corresponding di- and trichloroquinols, which may easily be separated by distillation with water, the former volatilising readily with the steam, while the latter remains in the residue.

Dichlorotoluquinol, $C^6HCl^2.CH^3.(OH)^2$, melts at 119°–121°, sublimes easily, and crystallises from hot water in feathery needles.

Trichlorotoluquinol crystallises from the solution left after distillation in long needle-shaped crystals. It melts at 211°–212°. This was the melting point found by Borgmann for his trichlorotoluquinol obtained from coal-tar cresol, which also agrees with this compound in the rest of its properties. It would, therefore, appear that the two compounds are identical, and hence that orthocresol is an essential constituent of the cresol from coal-tar.

The trichlorotoluquinone above mentioned is identical with that which Hayduck obtained by oxidising orthotoluidine-parasulphonic acid with potassium chlorate and hydrochloric acid (p. 2017).

Paracresol, on account of its structure, is incapable of conversion into a quinone; when treated with potassium chlorate and hydrochloric acid it yields nothing but dark-coloured uncrystallisable products.

Toluquinol, $C^7H^4O^2 = C^6H^3(CH^3)(OH)(OH)$ (Nietzki, *Ber.* x. 832, 1934; xi. 1278). This compound is formed by the action of sulphurous acid on the quinone, and crystallises from hot benzene in broad colourless needles, which melt at 124° and sublime partly without decomposition. It dissolves very readily in water (much more readily than the 6-carbon quinol), also in alcohol and ether, less readily in benzene. By slow oxidation it is converted into a quinhydrone, then into toluquinone. The quinhydrone is obtained in nearly black slender needles on mixing the aqueous

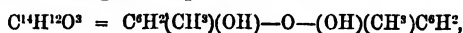
* In Southworth's paper these chlorinated quinones are distinguished as *chlor-ortho-* or *chlor-meta-*quinones, according to the cresol from which they are formed; but as there can be only one toluquinone, viz., that above formulated, these terms are not very appropriate.

solutions of molecular proportions of toluquinone and toluquinol, and agitating the yellow-brown liquid with ether. It melts at 52°.

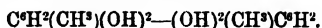
Toluquinol heated with *acetyl chloride* yields a diacetyl-derivative, which crystallises in large colourless plates, melts at 52°, and is converted by oxidising agents into the toluquinone.

Methyl-toluquinols.—A mixture of 12 pts. toluquinol and 30 pts. methyl iodide, heated for 12 hours at 100° with 8 pts. sodium hydroxide and 100 pts. methyl alcohol (or better with a solution of the calculated quantity of sodium in methyl alcohol), yields, as chief product, dimethyltoluquinol, $C^8H^{12}O$, together with a small quantity of monomethyltoluquinol, $C^8H^{10}O$. The latter melts at 72°, boils at 245°, dissolves in benzene, is but slightly volatile with water-vapour, and is converted by oxidation into toluquinone. *Dimethyltoluquinol* is slightly soluble in water, insoluble in aqueous potash, boils at 214°–218°, and likewise volatilises with water-vapour. By oxidation in glacial acetic acid (1 pt. of the quinol in 12 pts. acetic acid and 8 pts. water) with potassium dichromate (1·3 pt.) and sulphuric acid (3 pts.), it is converted (like ethyl-pyrogallol) into dihydroxymethyl-ditolylquinone, $C^{16}H^{16}O^4 = C^8H^2(CH^3)(OCH^3)_2O - O.(OCH^3)(CH^3)C^8H^2$. This last compound is nearly insoluble in water, but dissolves easily and with deep yellow-red colour in alcohol, ether, glacial acetic acid, and benzene, and crystallises in light brick-red or brown needles which melt at 153°, and sublime when cautiously heated above the melting point. By heating with aqueous ammonium sulphide it is converted into the corresponding hydro-compound, $C^{16}H^{18}O^4$, which crystallises from alcohol or benzene in slender needles melting at 173°; is nearly insoluble in acids, and is reconverted by oxidation into the quinone-like body.

When dimethyl-toluquinol is heated for several hours at 190° with eight or ten times its weight of strong hydrochloric acid, there is formed, together with methyl chloride, a substance having the composition



which is that of the anhydride of tetrahydroxyditolyl,



This anhydride is insoluble in water, soluble in alcohol and benzene, and crystallises from the latter in long flat needles containing benzene, from alcohol in colourless shining laminae which effloresce when heated. It unites with 1 mol. water, but it is not yet decided whether the water is taken up as water of crystallisation or whether the resulting hydrated body consists of *tetrahydroxyditolyl*. The anhydride heated with zinc-dust yields a semi-solid hydrocarbon having the odour of lemon-oil.

TOLUYL, $C^8H^7O = CH^3.C^6H^4.CO$. A monatomic acid radicle homologous with benzoyl, $C^6H^5.CO$. The same name is sometimes applied to the phenolic radicle, $C^6H^7 = CH^3.C^6H^4$, properly called **TOLYL**.

TOLUYL-BENZOIC ACID, $C^{15}H^{12}O^3 = CH^3.C^6H^4.CO.C^6H^4.CO^2H$. This acid is formed, together with ditolyl-ketone and diphenyl-ketone-dicarboxylic acid, $CO^2H.C^6H^4.CO.C^6H^4.CO^2H$, by the oxidation of ditolylmethane, $CH^3.C^6H^4.CH^2.C^6H^4.CH^3$, with a mixture of potassium chromate and dilute sulphuric acid (Weiler, *Ber.* vii. 1181); also, together with a dicarboxylic acid, $(C^6H^4.CO^2H)^2CO$, by oxidation of ditolyl-ketone with a mixture of chromic acid and glacial acetic acid (Ador a. Krafts, *Compt. rend.* lxxxv. 1163). It separates from the solutions of its salts on acidulation, as an extremely gelatinous precipitate, convertible by drying and trituration into a white powder, and crystallises from methyl alcohol or acetone in slender shining needles. It dissolves with great difficulty in cold, and only sparingly in hot water, but readily in methyl alcohol, ethyl alcohol, acetone, glacial acetic acid, potash, soda, and ammonia, less easily in benzene and in chloroform. Strong sulphuric acid dissolves it, even at ordinary temperatures, more readily at a gentle heat, forming a golden-yellow solution, from which it is thrown down by water as a white flocculent precipitate. It melts at 222°, and at a higher temperature undergoes partial carbonisation, and yields a white woolly sublimate (Weiler). According to Ador a. Krafts it melts at 228°, and sublimates without decomposition. Its *potassium salt*, $C^{15}H^{11}KO^3$, forms tufts of long white needles. The *sodium* and *ammonium salts* also crystallise well (Weiler).

TOLUYLENE. Syn. with **STILBENE** or **DIPHENYLETHYLENE**, $C^{14}H^{12} = C^8H^2(C^6H^5)^2$ (p. 675). The same name is sometimes applied in combination to the diatomic radicle C^8H^6 , more appropriately called *Tolyene* (q.v.)

TOLYL,* or *Methyl-phenyl*, $C^6H^7 = C^6H^4(CH^3)$. A monatomic radicle, meta-meric with BENZYL or PHENYL-METHYL, $CH^2(C^6H^5)$.

On DITOLYL, $CH^2.C^6H^4.C^6H^4.CH^3$, and its derivatives, see pp. 691-693.

TOLYL ALDEHYDE. Syn. with Toluic Aldehyde (p. 2027).

TOLYL CYANIDE, $C^6H^7.NC$, is converted into tolyl-thiocarbimide, $C^6H^7.N=CS$, and tolylthiocarbamide, $CS[NH(C^6H^7)]$, in the same manner as phenyl cyanide into the corresponding phenyl-compounds (p. 1546).

TOLYL-AMIDOGLYCOLL-AMIDES, -ANILIDES, and -TOLUIDES.
See GLYCOLLAMIDES (pp. 882, 883).

TOLYLAMINES, $C^6H^4(NH^2).CH^3$. Syn. with TOLUIDINES.

TOLYLARSENIC COMPOUNDS (La Coste a. Michaelis, *Ber.* xi. 1888).
Ortho-monotolylarsenious Chloride, $AsCl^2.C^6H^7$, is obtained by the action of (ortho)-mercury-ditolyl on arsenious chloride. It is a colourless liquid of faint odour, boiling at 264° - 265° , and may be distilled unchanged in an atmosphere of carbonic anhydride. It is converted by chlorine-gas into the tetrachloride $AsCl^4.C^6H^7$, a yellow liquid, which is decomposed by water into hydrochloric and monotolylarsenic acids. The corresponding para-compound is similarly obtained from (para)-mercury-ditolyl (m. p. 235°). It crystallises in colourless plates, which melt at 31° , and distils unchanged in an atmosphere of carbonic anhydride at 267° . The tetrachloride solidifies at a slightly reduced temperature; water decomposes it similarly to the ortho-compound. Both the above chlorides are converted by aqueous sodium carbonate into monotolylarsenoxides, $AsO.C^6H^7$. These are white powders, resembling arsenious oxide, easily soluble in hot alcohol, insoluble in ether.

The ortho-compound fuses at 146° , the para-compound at 156° . On raising the temperature, both undergo decomposition, with liberation of arsenious anhydride, the latter yielding tritolylarsine crystallising in plates (m. p. 129° - 130°).

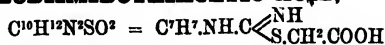
Orthomonotolylarsinic acid, $C^6H^7.AsO(OH)^2$, is the product of the action of water on the tetrachloride previously mentioned. It crystallises from its aqueous solution in slender needles, which melt at 160° to a colourless liquid. The para-compound, similarly prepared, crystallises from its aqueous solution in long needles, which on heating do not melt, but are decomposed at a temperature of 300° .

TOLYL-BUTYLENE, $C^{11}H^{14} = CH^2.C^6H^4.CH^2.C^6H^5$, is formed, together with diallyl and dixyl, by heating 1 mol. metaxyl chloride, $CH^2.C^6H^4.CH^2Cl$, 1 mol. allyl iodide and 4 at. sodium on the water-bath till reaction begins, then cooling the mixture to prevent the action from becoming too strong, and again heating it on the water-bath for six or eight hours. The pure tolyl-butylene, separated from the crude product by filtration and fractional distillation, is a limpid liquid having a sweetish odour, boiling at 195° , and uniting with bromine to a colourless oil which does not solidify at -10° (Aronheim, *Ber.* ix. 1789).

TOLYL-CARBAMIDE, or TOLYL-UREA, $C^6H^{10}N^2O = NH^2.CO.NH(C^6H^7)$. Sell obtained a monotolyl-carbamide by the action of potassium cyanate on toluidine sulphate, and described it as crystallising in white needles, and decomposing at 158° into ammonia and ditolyl-carbamide (i. 872). Schwebel (*Ber.* xi. 1128) obtains a tolyl-carbamide, together with tolyl-hydantoic acid, tolyl-hydantoin (*q.v.*), and toluidine, by fusing tolylglycocine with urea. The tolylcarbamide thus obtained crystallises in silvery needles, insoluble in water, not attacked by acids or alkalis, and decomposing at about 200° . Lastly, a tolyl-carbamide melting at 182° is obtained by the reaction described in the following article. As all these three products were obtained from ordinary *p*-toluidine, it is probable that the differences between them are due to different degrees of purity.

TOLYL-CARBINOX, $C^6H^{10}O = CH^2.C^6H^4.CH^2OH$. Syn. with XYLAL ALCOHOL (*q.v.*)

TOLYLCARBODIIMIDOTHIAcETIC ACID,



is formed, like the corresponding phenyl-compound (p. 1555), by the action of monochloroacetic acid on *p*-toluidine thiocyanate, or on a mixture of a metallic thiocyanate

* There is some confusion in the use of this term, as it is applied sometimes, as above, to the 7-carbon radicle, methyl-phenyl, $CH^2.C^6H^4-$, sometimes to the 8-carbon radicle, $C^6H^7 = CH^2.C^6H^4.CH^2-$; but this latter, being derived from xylene, is better called 'xylyl,' e.g. $C^6H^7Br = CH^2.C^6H^4.CH^2Br$ = bromoxylene or xylyl bromide.

with toluidine. It melts at 176° – 182° , and is resolved by prolonged heating with sulphuric acid into thioglycollic acid and *p*-tolyl-carbamide, melting at 182° .



(Nencki, *J. pr. Chem.* [2], xvi. 1; Jäger, *ibid.* 17).

TOLYL-CHLORACETAMIDE, $\text{CH}^2\text{Cl.CO.NH}(\text{C}^6\text{H}^4.\text{CH}^2)$. See ACETAMIDES (p. 7).

Di-TOLYLDIAZINS, $\text{C}^6\text{H}^4\text{N}^2 = \text{CH}^2.\text{C}^6\text{H}^4.\text{N}=\text{N}.\text{C}^6\text{H}^4.\text{CH}^2$. *Azotoluenes*.—The *ortho*- and *para*-modifications (α and β , vi. 265; vii. 1163) are formed by reduction of liquid and solid nitrotoluene respectively with sodium-amalgam. The *para*-compound is however more readily obtained in the pure state by oxidation of *p*-ditolyl-hydrazine (p. 1057). It melts at 144° – 145° , sublimes with decomposition, and is less soluble in alcohol than the *ortho*-compound (Petrieff, *Ber.* vi. 556). It may also be prepared in considerable quantity by oxidation of *p*-toluidine: (a). With bleaching powder in presence of chloroform (R. Schmitt, *J. pr. Chem.* [2], xviii. 196); (b). By drenching the toluidine with a quantity of hydrochloric acid not sufficient to dissolve it completely, and then treating it with a solution of potassium permanganate. The ethereal extract of the resulting mass leaves on evaporation a black mass, from which petroleum-ether extracts a substance crystallising in reddish needles, having the composition and melting point of ditolyl-*p*-diazin; and the second and third ethereal extracts of the crude product yield crystals melting at 244° – 245° , and having the composition of *ditolyl-ditolylene-tetrazin*, $\text{C}^{12}\text{H}^{20}\text{N}^4$ (Barsilowsky, *Ber.* vi. 1209; xi. 2153). See p. 2031.

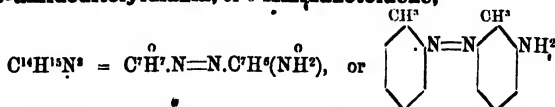
Bromo-*p*-ditolyl-diazin, obtained by direct bromination, crystallises in concentric groups of needles, which dissolve with difficulty in alcohol and ether, easily in chloroform and benzene; it melts at 136° , and sublimes without decomposition at a higher temperature.

Mononitro-*p*-ditolyl-diazin (m. p. 76°) and the **dinitro-compound** (m. p. 1100° ?) are formed by heating the paradiazin with nitric acid of sp. gr. 1.4, the dinitro-compound separating from an alcoholic solution on cooling in yellow needles, and the mononitro-compound from this mother-liquor in white needles. Stronger nitric acid of sp. gr. 1.54 converts the paradiazin into a trinitro-ditolyl-oxydiazin, $\text{C}^6\text{H}^{11}(\text{NO}_2)^3\text{N}^2\text{O}$, melting at 201° (Petrieff); compare vii. 1163.

Orthoditolyl-diazin may be advantageously prepared by oxidising *o*-toluidine with potassium permanganate, the yield amounting to 30 per cent. of the toluidine used. It is nearly insoluble in water, but dissolves readily in alcohol, ether, benzene, carbon sulphide, and chloroform, and crystallises in well-defined prisms having a fine red colour, and melting at 55° . It volatilises readily with water-vapour, is not attacked by boiling soda-ley, but dissolves in strong sulphuric acid, and is precipitated from the solution by water, apparently unchanged. It is not altered (neither is the *para*-compound) by further treatment with potassium permanganate (Hoogewerff a. van Dorp, *Ber.* xi. 1202).

Metaditolyl-diazin, prepared by reduction of metanitrotoluene with sodium-amalgam, or better with zinc-dust and alcoholic potash, separates from alcoholic solution in large orange-red crystals very much like those of diphenyl-diazin (azo-benzene). It melts at 54° (Barsilowsky, *Ber.* x. 2098, 2240). A. Goldschmidt (*ibid.* xi. 1625) obtains the same compound, together with metatoluidine, by distilling the crude product of the action of alcoholic potash on metanitrotoluene, and finds that it crystallises in large red tablets melting at 51° , insoluble in water, easily soluble in alcohol and benzene, deliquescent in ether into symmetrical metaditolyl-hydrazine.

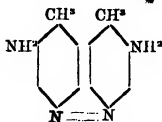
Ortho-amidoditolyl-diazin, or *o*-Amidazotoluene,



This compound is formed by treating orthotoluidine floating on a saturated solution of common salt with nitrous acid; and on washing the resulting thick dark-brown oil with soda-ley, and treating it with hot dilute hydrochloric acid, the liquid on cooling, especially after addition of strong hydrochloric acid, deposits laminæ of *amidoditolyl-diazin hydrochloride*, which after drying in a vacuum has the composition $\text{C}^6\text{H}^{12}\text{N}^2.\text{HCl}$; it gives off hydrochloric acid at 100° , dissolves sparingly in cold water, easily in water acidulated with hydrochloric acid, and in alcohol. The base separated by ammonia forms thin laminæ or tabular crystals having a golden lustre

and blue surface-shimmer, melts at 100° , and dissolves readily in alcohol and ether, but is insoluble in water. Its salts have an orange-yellow colour, and are decomposed by water; the *silver salt* forms golden-yellow easily decomposable laminae; the *platinochloride*, thin brown plates, which when dried at 100° have the composition $(C^1H^{15}N^3, HCl)^2PtCl^4$ (Nietzky, *Ber.* x. 662, 1155).

Ortho-amidotolyldiazin, $C^6H^4(NH^2).N^2.C^6H^7$



is very much like ortho-amidotolyl-*o*-tolylidiazin; it melts at 127° – 128° , and forms salts which have a steel-blue lustre and exhibit a crimson colour in acid solution. The *hydrochloride*, $C^1H^{15}N^3, HCl$, crystallises in cinnabar-red needles; the *platinochloride* is insoluble in water, and contains 5 percent. water, which it gives off at 130° .

Amidophenylparatolylidiazin, $C^6H^4(NH^2).N^2.C^6H^7$, crystallises in needles an inch long having a dark yellow colour and blue shimmer; melts at 147° ; forms a rose-coloured hydrochloride crystallising in nacreous rhombic tablets, and a *platinochloride* which crystallises in brown needles, and when dried at 130° has the composition $(C^1H^{15}N^3, HCl)^2PtCl^4$. The *silver salt*, $(C^1H^{15}N^3)^2AgOH$ (at 100°), crystallises in golden-yellow scales.

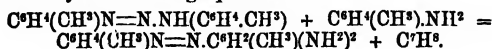
Metamidoditolylidiazin (metamidazotoluene) is easily formed by the action of nitrous acid on metatolylamine. Its salts are but slightly soluble in water; the hydrochloride crystallises from alcohol containing hydrochloric acid in long dark steel-blue needles which are decomposed by water; the acid solutions of the salts have a fine red colour. The base itself forms golden-yellow needles melting at 80° . The *platinochloride*, $(C^1H^{15}N^3, HCl)^2PtCl^4$ (at 130°), forms yellow, metallicly lustrous laminae, nearly insoluble in water and in alcohol. *Paratolylidiazin-tolylamide* and *metatoluidine hydrochloride* react in alcoholic solution, with elimination of *p*-toluidine, forming metamidotolylparatolylidiazin, which crystallises in yellow laminae melting at 127° . The *hydrochloride* of this base consists of stellate groups of steel-blue laminae; the *platinochloride*, $(C^1H^{15}N^3, HCl)^2PtCl^4$, of sparingly soluble needles having a bronze lustre.

Ortho-amidoditolylidiazin and aniline hydrochloride heated with alcohol at 160° yield a red dye-stuff resembling saffranin, which dissolves in water with red, in strong hydrochloric acid with deep blue colour, changing to red on dilution. The *p-o*-compound yields a violet colouring matter; the tolylphenyl-compound a violet colour with ortho-, a blue-violet with *p*-toluidine. These colouring matters are reduced by zinc, yielding colourless solutions, which quickly become coloured on exposure to the air.

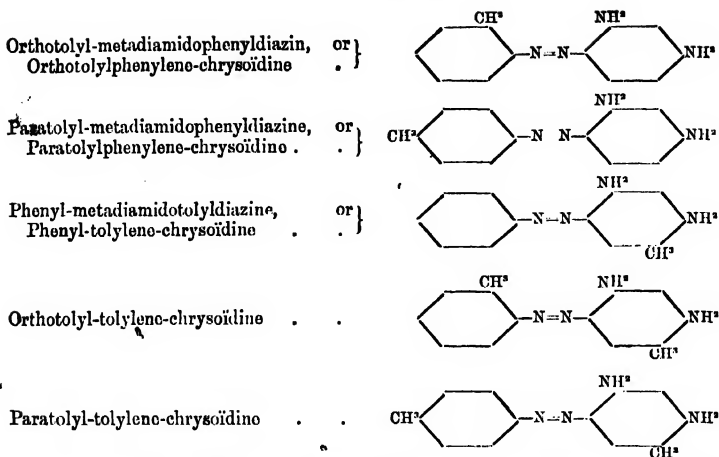
The mixture of bases obtained by reduction of metamidoditolylidiazin gave by oxidation, after addition of a small quantity of orthotoluidine, the green coloration characteristic of (*m-o*)-tolylenediamine (vii. 1180). Hence, in the bodies above described the substituted groups probably stand in the positions 1 (methyl), 2, 5 (Nietzki, *loc. cit.*)

Tolylamidotolylidiazin, $C^1H^{15}N^3 = C^6H^4N=N.NH(C^6H^7)$. *Diazotoluene-amidotoluene* (Nietzki, *Ber.* x. 662, 1155).—This compound is formed by dissolving 2 pts. paratoluidine and 1 pt. amyl nitrite in 8 to 10 pts. ether, and leaving the solution to evaporate in a moderately warm place. It then remains as a crystalline pulp, which may be purified by washing with alcohol. When mixed in alcoholic solution with hydrochloride of aniline or orthotoluidine (not of paratoluidine), it unites with those compounds, forming salts of diamidotolylidiazins—bodies homologous with *chrysoïdine* or *phenyl-m-diamidophenylidiazin*, $C^6H^4N=N.C^6H^4(NH^2)^2$ (p. 469).

To prepare these compounds, a mixture of tolyl-tolylamido-diazin with somewhat more than the theoretical quantity of aniline hydrochloride or orthotoluidine hydrochloride is drenched an eight to ten-fold quantity of alcohol, whereupon the reaction takes place attended with rise of temperature, and is completed in three or four hours. The product boiled with dilute hydrochloric acid yields a solution which on cooling deposits the hydrochloride of the diamido-diazin compound. The reaction may perhaps be represented by the following equation:

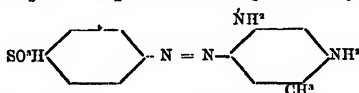


The same compounds may be prepared (like *chrysoïdine*) by the action of tolyldiazin salts (diazotoluene salts) on phenylene- and tolylene-diamines (p. 470). The following have been obtained by O. N. Witt (*Chem. Soc. J.* xxxv. 181):



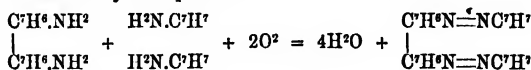
The hydrochlorides of these bases form splendid yellow and orange dye-stuffs, known commercially as 'chrysoïdines.'

Phenyl-tolylene-chrysoïdinesulphonic acid is represented by the formula :

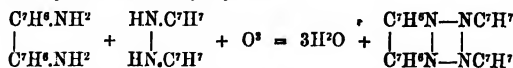


Ditolyl-ditolylene-tetrazin, $C^{20}H^{20}N^4 = C^7H^7N=N.C^7H^6.C^7H^6.N=NC^7H^7$
 $C^7H^6.N.N.C^7H^7$
 or $\begin{array}{|c|} \hline C^7H^6.N.N.C^7H^7 \\ \hline \end{array}$ (Barsilowsky, *Ber.* xi. 2153). This is the compound formed,

together with *p*-ditolyl-diazin, by oxidation of *p*-toluidine with potassium permanganate (p. 1996). Its formation is explained by Barsilowsky as follows: 2 mols. toluidine are first converted into ditolyl-hydrazine, $C^7H^7NH.NH.C^7H^7$, part of which is oxidised to *p*-tolylldiazin, while another portion is converted into the isomeric toluidine, $NH^2(C^7H^7).C^7H^7NH^2$, a molecule of which unites either with 2 mols. toluidine, as indicated by the equation :



or with 1 mol. of symmetrical ditolyl-hydrazine :



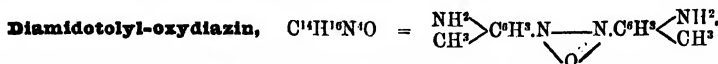
This compound, treated with chlorine or bromine, yields nothing but resinous products. The *hydrazine*, $C^{20}H^{20}N^4$, prepared from it, is dissolved by acids and precipitated from the solutions by alkalis without alteration. Its alcoholic solution treated with acids forms saline precipitates, of which those formed by sulphuric, hydrochloric, and nitric acid cannot be obtained in the crystalline state. Those formed with organic acids are, however, more stable, the most characteristic being the *oxalate*, $C^{20}H^{20}N^4.C^2H^2O^4 + H^2O$, which is crystalline, slightly soluble in water, easily soluble in alcohol, especially with aid of heat, but decomposes when heated in an air-bath even below 100° , and gives up part of its acid even to water. With *methyl* or *ethyl iodide* the hydrazine forms only resinous products; with *acetyl chloride* it forms a crystallisable body, consisting either of $C^{14}H^{14}N^2(C^2H^3O)^2$ or $C^{20}H^{20}N^4(C^2H^3O)^4$.

Tolyl-oxytolylldiazin, or **Oxyazotoluene**, $C^7H^7N=N.OC^7H^7$, formed, together with two other compounds, by the action of paratoluidine acetate on nitroso-phenol, crystallises in orange-yellow prisms, somewhat soluble in hot water, and melting at 151° . It possesses acid properties, and forms a silver salt which crystallises in shining orange-coloured needles.

Ditolyloxydiazin, $C^{14}H^{14}N^2O = C^6H^5.N.O.NC^6H^5$. *Azoxytoluene*.—This compound, formed, together with ditolyldiazin, by the action of sodium-amalgam on nitrotoluene in alcoholic solution, crystallises, according to Melms, in yellow needles melting at 70° ; according to Petrieff, in large laminae melting at 57° (see vii. 1163).*

Monobromo-p-ditolyloxydiazin (p. 1163), and the corresponding dibromo-compound, are obtained by dissolving *p*-ditolyloxydiazin in bromine not cooled. The latter is slightly soluble in alcohol, and crystallises in needles melting at 138° (Petrieff, Ber. vi. 556).

Mononitro-p-ditolyloxydiazin, melting at 84° , and the dinitro-compound at 145° , are obtained by heating *p*-ditolyloxydiazin (m. p. 59°) with nitric acid of sp. gr. 1.4. Both crystallise in yellow needles, and may be separated by alcohol, in which the dinitro-compound is insoluble (Petrieff, loc. cit.)



Azoxytoluidine (E. Buckney, Ber. xi. 1451).—This base is formed as a thick pulp on gradually mixing a concentrated solution of nitro-*p*-toluidine in absolute alcohol with very small pieces of sodium-amalgam (50 g. substance being reduced in $1\frac{1}{2}$ to 2 days). It may be purified by recrystallisation from a large quantity of water, and then forms small yellow needles melting at 148° , slightly soluble in cold, more freely in hot water and alcohol. With strong hydrochloric acid it forms a sparingly soluble yellow-brown hydrochloride, $C^{14}H^{16}N^4O, 2HCl$, from the aqueous solution of which platonic chloride throws down the yellow double salt, $C^{14}H^{16}N^4O, 2HCl, PtCl_4$.

Diamidotolyldiazin, $\begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array} > C^6H^5.N = N.C^6H^5 < \begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array}$, and the corresponding *hydrazine*, $\begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array} > C^6H^5.NH.NH.C^6H^5 < \begin{array}{c} \text{NH}_2 \\ \text{CH}_3 \end{array}$, are formed simultaneously by the action of sodium-amalgam on the oxydiazin in alcoholic solution, and may be separated by their difference of solubility in alcohol. The *diazin*, also called *azotoluidine*, is easily soluble in alcohol, is precipitated from the alcoholic solution by water, and crystallises in red needles melting at 159° . The *hydrazine*, $C^{14}H^{18}N^4$ (hydrazotoluene), crystallises in small colourless plates melting at 180° , nearly insoluble in water, ether, and cold alcohol, sparingly soluble in hot alcohol, and easily oxidised in alcoholic solution (even by heating in contact with the air to diamidotolyldiazin).

Ditolylhydrazines, $C^{14}H^{16}N^2$. The symmetrical modifications of these $C^6H^5.NH$ compounds, $\begin{array}{c} | \\ C^6H^5.NH \\ | \end{array}$, also called *hydrazotoluenes*, are formed by the action of sodium-amalgam or ammonium sulphide on the corresponding ditolyldiazins or -oxydiazins (vii. 1163). The *ortho*-compound (m. p. 165°) is permanent in the dry state when kept from contact with the air, but is converted into ditolyldiazin or -oxydiazin when dissolved in alcohol or water. When dry chlorine oxide gas, Cl_2O , is passed into its ethereal solution, a white powder is formed, whose aqueous solution gives with the nitrates of silver and copper insoluble precipitates from which alkalis separate a body crystallising in racemous laminae, sparingly soluble in water, easily in alcohol and ether, and appearing from the analysis of its hydrochloride, $C^{14}H^{16}N^2.HCl$, to be an isomeric toluidine or diamidoditolyloxy, $C^{14}H^{16}N^2(NH_2)^2$ (vii. 1163). At the same time ditolyloxydiazin and an addition-product are formed, the reaction being represented by the equation:



(Petrieff, Ber. vi. 556).

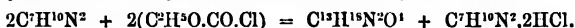
Metaditolyloxydiazine (symmetrical), obtained by the action of alcoholic ammonium sulphide on *m*-ditolyldiazin, is easily alterable in contact with the air, and is converted by addition of sulphuric acid to its solution in dilute alcohol, into *m*-toluidine sulphate, $[C^6H^4(CH_3)NH_2]^2H^+SO_4^{2-}$, which is easily soluble in water, insoluble in alcohol, and crystallises in laminae having a satiny lustre. *m*-Toluidine is separated from this salt by ammonia as an oil which solidifies at low temperatures, forms salts with hydrochloric and nitric acids, and is coloured blue by ferric chloride (A. Goldschmidt, Ber. xi. 1625).

* As both Melms and Petrieff operated on solid nitrotoluene, the great difference between the melting points of the ditolyldiazins which they obtained is not easy to account for, except on the supposition that Melms' product was contaminated with ditolyldiazin, which melts at 137° .

TOLYLDIPHENYL-METHANE, $C^{20}H^{18} = CH(C^6H^5)(C^6H^5)^2$ (E. and O. Fischer, *Liebig's Annalen*, cxciv. 282). This hydrocarbon is prepared by the action of boiling alcohol on diazoleucaniline chloride (p. 1178). When recrystallised from methyl alcohol, it forms spherical groups of prisms easily soluble in ether, benzene, and ligroin, less easily in cold alcohol and wood-spirit; it melts at $59^\circ-59.5^\circ$, and boils without decomposition at a temperature above 360° . Nitric acid converts it into a number of nitro-compounds, one of which, when treated with zinc-dust and glacial acetic acid, yields leucaniline.

Tolyldiphenyl Carbinol, $C^{20}H^{18}O = (C^6H^5)(C^6H^5)^2COH$, obtained by oxidising the hydrocarbon dissolved in glacial acetic acid with chromic acid, crystallises from ligroin in six-sided prisms or tables, melts at 150° , dissolves easily in ether, alcohol, and benzene, less easily in ligroin, and boils without decomposition.

TOLYLENE-CARBAMATE, ETHYLIC or **TOLYLENE-URETHANE**, $C^{11}H^{10}N^2O = C^7H^5 \begin{smallmatrix} \text{NH.CO.O}C^2H^5 \\ \text{NH.CO.O}C^2H^5 \end{smallmatrix}$ is formed, together with tolylene-diamine hydrochloride, by the action of ethylic chlorocarbonate on tolylene-diamine:



On dissolving the product in water, the urethane separates first in fine crystals, which may be purified by treatment with animal charcoal and recrystallisation from alcohol. It forms dazzling white needles having a silky lustre, soluble in ether, and melting at 137° . On distillation, the greater part passes over unaltered, but the remainder is decomposed into alcohol and tolylene isocyanate, $C^7H^5(NCO)^2$. The same compound is obtained more abundantly by distilling the urethane with phosphoric anhydride, and passes over as a strongly refractive liquid having a fearfully pungent and tear-exciting odour. In contact with ether, this liquid quickly solidifies, and therefore appears, like many other cyanates, to pass into a polymeric modification. The solid body thus formed consists of stellate groups of yellow transparent crystals melting at 95° , and reconverted by alcohol into tolylene-urethane.

TOLYLENE-DIAMINES, $C^7H^5(NH^2)^2.CH^3$. Syn. with DIAMIDO-TOLUENES (pp. 2003-2005).

TOLYLENE - DICARBAMIDE, or **TOLYLENE - DIUREA**, $C^7H^5(NH.CO.NH^2)^2$, which Strauss obtained, by adding tolylene-diamine to a cooled solution of potassium cyanate (vi. 1117), is also formed by the action of ammonia on tolylene-isocyanate. It forms shining crystalline scales sparingly soluble in alcohol and in boiling water, melting at 220° . When heated with ethyl iodide at 110° , it is converted into diethyl-tolylene-carbamide, a yellowish body soluble in alcohol and ether, melting at 175° (Lussy, *Ber.* viii. 291).

TOLYLENE-THIOCARBAMIDE, $C^7H^5N^2S = N^2(C^7H^5)(CS)H^2$, is formed by the action of potassium thiocyanate on a warm aqueous solution of tolylene-diamine, the immediate product of the reaction being tolylene-diamine thiocyanate, which is subsequently converted into the thiocarbamide (Lussy, p. 2003).

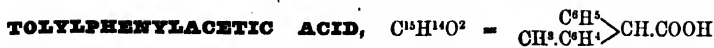
On **TOLYLENE-DITHIOCARBAMIDE**, $C^7H^5(NH.CS.NH^2)^2$, and its Ethyl- and Phenyl-derivatives, see CARBAMIDES (p. 399).

TOLYL-GLYCOCINE, $C^9H^{11}NO^2 = C^7H^5.NH.CH^2.COOH$. This compound, which P. J. Meyer obtained by heating *p*-toluidine with monochloroacetic acid (p. 881), may also be prepared by prolonged heating of toluidine chloracetate with water. When purified by recrystallisation from hot water (which is attended with partial decomposition), it crystallises in slender colourless felted needles, and after a further crystallisation in long straw-yellow needles which melt, with decomposition, at $166^\circ-168^\circ$ (Meyer's product melted at about 145° , and decomposed at about 170°). Its solution in strong hydrochloric acid gives a crystalline precipitate with platinic chloride, amorphous precipitates with mercuric chloride and stannous chloride, green with cupric sulphate (Schwebel, *Ber.* x. 2045).

TOLYL-HYDANTOIC ACID, $\begin{smallmatrix} CH^2.N(C^7H^5).CO.NH^2 \\ | \\ COOH \end{smallmatrix}$, and **TOLYL-HYDANTOIN**, $\begin{smallmatrix} CH^2.N(C^7H^5) \\ | \\ CO-NH \end{smallmatrix} \rangle CO$. See HYDANTOIC ACID (p. 1046).

TOLYL-HYDRAZINE, $CH^2.C^6H^4.NH.NH^2$. See HYDRAZINES (p. 1057).

TOLYL-OXAMETHANE, $CH^2.C^6H^4.CO.NH.CO^2C^2H^5$. See OXAMIC ETHERS (p. 1457).



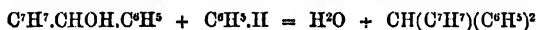
(Tanisch, *Ber.* x. 996). This acid, homologous with diphenyl-acetic acid (p. 665), is produced by the action of toluene and zinc-dust on phenyl-bromacetic acid, the product consisting mainly of *p*-tolyl-phenyl-acetic acid, with a smaller quantity of the ortho-acid.

Paratolyl-phenylacetic acid dissolves sparingly in cold water, a little more freely in boiling water, readily in alcohol, ether, chloroform, and carbon sulphide, and crystallises in nearly rectangular plates, melting at 115° , and subliming, when more strongly heated, in oily drops, which gradually solidify and then melt at 108° – 110° .

The *potassium salt* crystallises from a concentrated solution in clear monoclinic plates, containing 4 mol. of water. The *sodium salt* is very soluble, and forms needles with 6 mol. of water. The *barium salt* could be obtained only as a resinous mass, and the *calcium salt*, which is well adapted for the purification of the acid, is very sparingly soluble in cold and hot water, and crystallises from dilute hot alcohol in glistening needles containing 2 mols. of water. The salts of *lead*, *copper*, *silver*, and *zinc* are precipitates; the first crystallises from hot alcohol in needles; the copper and zinc salts dissolve also in alcohol, and more freely in ether-alcohol, separating in viscid drops, which gradually solidify. The *methyl-ether* is a thick oil, and the *ethyl-ether* crystallises from alcohol in plates melting at 34° . The *amide* forms needles, which are grouped in warty masses and melt at 151° . The soluble salts of the acid are decomposed by carbon dioxide. Chromic acid solution oxidises the acid to paratolylphenyl ketone and parabenzoylbenzoic acid.

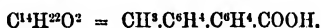
On purifying the crude acid by crystallisation from alcohol, a mother-liquor is obtained, containing an oily acid, which cannot be crystallised, and consists of a mixture of the para- and ortho-acids. A separation of these could not be effected, but their presence was proved by oxidation, a mixture of para- and ortho-benzoylbenzoic acid being thereby produced.

***p*-TOLYLPHENYL-CARBINOL**, $C^{14}H^{16}O = CH^3.C^6H^4.CHOH.C^6H^5$, obtained by the action of sodium-amalgam on *p*-tolylphenyl ketone (p. 1154), forms, when purified by crystallisation from ligroin, concentric groups of colourless needles having a silky lustre and melting at 52° – 53° . A mixture of tolylphenyl-carbinol and benzene heated with phosphoric anhydride yields tolyldiphenyl-methane (p. 2036):



(E. and O. Fischer, *Liebig's Annalen*, xciv. 265).

TOLYPHENYL-CARBOXYLIC ACID,



produced by incomplete oxidation of solid ditolyl with chromic acid, melts at 243° – 244° (Carnelley: see DITOLYL, p. 691).

TOLYPHENYL-GUANIDINE, $CH^3(C^6H^5)(C^6H^7)N^3$, and **DITOLYL-GUANIDINE**, $CH^3(C^6H^7)^2N^3$. See GUANIDINES (p. 909).

TOLYPHENYL KETONES, $C^{14}H^{12}O = CH^3.C^6H^4.CO.C^6H^5$ (Plascuda a. Zincke, *Ber.* vii. 375). The preparation and properties of the para- and ortho-modifications of these bodies and their chlorinated derivatives have already been described (pp. 1154–1156); also their oxidation to para- and ortho-benzoylbenzoic acid respectively (p. 309).

Nitro-derivatives.—*Mononitrotolylphenyl Ketone*, $CH^3.C^6H^4.CO.C^6H^4(NO^2)$, produced by the action of fuming nitric acid on solid tolylphenyl ketone, is identical with the nitromethylbenzophenone obtained by the action of dilute nitric acid on benzyl-toluene (vii. 183). It crystallises from hot alcohol in broad shining laminae or groups of needles, melts at 126° – 127° , and sublimes easily in shining laminae or groups of needles, dissolves readily in chloroform, benzene, and hot acetic acid. By boiling its solution in glacial acetic acid with chromic acid, it is oxidised to benzoic acid and metanitrobenzoic acid (m. p. 140°). The greater part of the nitro-ketone is, however, completely burnt in this process, and the first product of the oxidation, viz. *mononitrobenzoylbenzoic acid*, has not been obtained.

Dinitrotolylphenyl Ketone, $C^{14}H^{10}(NO^2)^2O$, is produced by prolonged boiling of dinitrobenzyl-toluene (p. 183) with nitric acid of sp. gr. 1.4, or by heating its solution in glacial acetic acid with chromic acid. It crystallises from acetic acid in thick yellowish needles, from alcohol in silky laminae; melts at 126° – 127° ; decomposes at a higher temperature, without subliming; dissolves with moderate facility in benzene

and in chloroform, less easily in ether. By oxidation it yields paranitrobenzoic acid and dinitrobenzoylbenzoic acid, $C^1H^4(NO^2)^2O^2$.

Trinitrotolylphenyl Ketone, $C^1H^9(NO^2)^3O$, obtained by adding solid tolylphenyl ketone or its mono- or di-nitro-derivative to a mixture of nitric and sulphuric acids, crystallises from alcohol or from glacial acetic acid in small well-defined yellowish prisms, melts at 165° , and decomposes without subliming at a higher temperature.

The nitro-derivatives of orthotolylphenyl ketone are uncrystallisable resins.

TOLYLPHENYL PINACOLINS, $C^{28}H^{21}O$. See KETONES (p. 1155).

TOLYLPHENYL-SULPHONE, $C^7H^7.8O^2.C^6H^5$. See SULPHONES (p. 1855).

TOLYL-SILICONIC ACID, $C^7H^7.SiO^2H$. An acid produced by the action of ammonia on silico-tolyl chloride, $C^7H^7SiCl^3$ (p. 1794).

TOLYL-SULPHOXIDES (p. 1856).

TOLYL-TRIOHYDANTOÏN, $CS \begin{array}{l} \text{NH} \text{---} \text{CH}^2 \\ \diagdown \quad | \\ \text{N}(C^7H^7) \text{---} \text{CO} \end{array}$. See HYDANTOÏN (p. 1047).

TOLYL-TOLYLENE-CHRYSOÏDINE, $C^{14}H^{16}N^4 = C^7H^7.N = N.C^7H^5(NH^2)^2$. A homologue of chrysoïdine, more properly called *Diamidazotoluene* or *Tolyldiamido-tolyldiazin* (p. 470). It crystallises in stellate groups of orange-coloured needles, easily soluble in alcohol and ether, almost insoluble in water. The *hydrochloride*, $C^{14}H^{16}N^4.HCl$, crystallises in red needles, and yields a crimson platinumchloride (Hofmann, *Ber.* x. 218).

TOPAZ. The following analyses of topaz have been published by H. Klemm (*Jahrb. f. Min.* 1874, 189).

1. Pyrophasite. 2. Topaz from Miask. 3. From Freiberg. 4. Values deduced from the formula $5Al^2O^3.SiO^2 + SiF^4$, the fluorides being reckoned as the equivalent quantities of oxides:

	1	2	3	4
F	17.106	17.167	17.447	17.50
SiO ²	33.643	33.469	33.323	33.16
Al ² O ³	56.213	56.529	56.350	56.70

On the Crystalline forms of Topaz, see E. Bertrand (*Zeitschr. Kryst.* i. 297); Laspeyres (*ibid.* 347); Jeremjew (*ibid.* ii. 504); Seligmann (*ibid.* iii. 30); also *Jahresh. f. Chem.* 1877, 1305; 1877, 1237. On Minerals enclosed in Topaz, see Hartley (*Chem. Soc. J.* xxxi. 241). On Corrosion-figures of Topaz, see Baumhauer (*Jahrb. f. Min.* 1876, 1).

On the Decomposition of Topaz at high temperatures, see SILICATES (p. 1792).

TOPAZOLITE. Crystals of this mineral (a variety of garnet) from the trap-rocks of New Haven, Connecticut, are described by E. S. Dana (*Sill. Am. J.* [3], xiv. 215; *Jahresh. f. Chem.* 1877, 1313).

TORBANITE. On the supposed formation of this carbonaceous mineral from petroleum, see W. Skey (*Chem. News*, xxxi. 16).

TOURMALIN. Green tourmalin from Campolongo has been analysed by Th. Engelmann (*Zeitschr. Kryst.* iii. 312) with the following result:

Fl	SiO ²	Al ² O ³	Be ² O ³	FeO	MnO	MgO	Na ² O	K ² O	H ² O
0.60	39.26	38.33	9.40	4.51	1.12	1.02	2.43	0.38	2.41 = 99.46

Sp. gr. of opaque crystals from Campolongo, 2.802; of transparent crystals from the same locality, 2.969; of crystals from the Binnenthal, 2.925.

Intergrowths between tourmalin and orthoclase are described by E. H. Williams (*Sill. Am. J.* [3], xi. 273). The tourmalin crystals, which are imbedded in quartz or orthoclase, were found in a quarry near Port Henry, New York.

The Corrosion-figures of tourmalin and topaz have been examined by H. Baumhauer (*Jahrb. f. Min.* 1876, 1).

TRACHYTE. *Analyses*. 1. From Gladstone in Queensland, resembling that of the Puy-de-Dôme (Daintree, *Geol. Soc. Qu. J.* xxviii. 271). (2-5). *Augite trachytes* from the Andes. 2. From Tunguragua: black, very finely crystalline ground-mass enclosing plagioclases, augite and magnetite. 3. Tunguragua: red, porous ground-mass enclosing numerous plagioclases and short prismatic augites; magnetite is wanting, having probably been converted into ferric oxide: hence the red coloration. 4. Pichincha, 4,860 meters above the sea-level: greenish-black, finely crystalline ground-mass, enclosing small augites and magnetite, also plagioclases containing

cavities and enclosed liquids. *u.* Cachofruto, near Marmato: grey, very hard ground-mass enclosing tabular plagioclases, with small quantities of augite and magnetite (Artopé, *Jahrb. f. Min.* 1874, 93). 6. Trachyte from Wolferdingen, in the Westerwald (Hilger, *ibid.* 1877, 421). (7-9). Trachytes from the neighbourhood of Gleichenberg (E. Ludwig, *Min. Mitth.* 1877, 276). 7. Quartz-trachyte from the Schaufelgraben, near Gleichenberg, analysed by H. Frisch; sanidine and quartz in a dull, somewhat porous ground-mass; on decomposition it yielded 27.14 per cent. quartz. 8. Trachyte, north of Gleichenberg, analysed by L. Smita. 9. Trachyte from the Schuh Villa, Gleichenberg, distinguished from No. 2 by a small amount of spathic iron ore; analyses by J. Utschik. 10. Quartz-trachyte from the Tardree Mountain, County of Antrim, Ireland. The analyses and the microscopic examination indicate the presence of 62 per cent. sanidine and 38 per cent. quartz and tridymite. The sanidine contains exactly equivalent quantities of potassium and sodium (A. v. Lasaulx, *Min. Pet. Mitth.* [2], i. 410). 11. Sanidine-plagioclase trachyte from the Volcano of Ferra in Sardinia. 12. Sanidine-augite trachyte from the same locality (C. Dölter, *Jahresb. f. Chem.* 1878, 1287). 13. Quartziferous Sanidine-trachyte from Nagy-Kövesd: red-brown ground-mass, much decomposed and rich in ferric oxide; contains numerous quartz-grains and feldspars enclosing laminae of mica and hornblende (Dölter, *Jahrb. f. Min.* 1875, 95). 14 and 15. Hornfels-trachyte from Markt Tüffer in Styria. 14. Red. 15. Green; sp. gr. 2.75 (R. v. Drasche (*ibid.* 1873, 768). 16. Trachyte-tufa from Wöllan in Styria, sp. gr. 2.51 (v. Drasche, *loc. cit.*)

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	CaO	MgO	K ² O	Na ² O	H ² O	CO ²	
1.	67.80	14.67	5.35	—	—	—	—	5.65	4.60	1.30	—	= 99.37
2.	66.06	15.64	—	3.90	0.71	4.55	2.57	2.36	4.00	0.30	—	= 100.09
3.	58.35	16.74	—	6.71	0.54	6.81	4.84	1.18	4.69	0.31	—	= 100.17
4.	62.35	17.32	—	4.51	0.04	5.43	3.60	3.13	4.29	0.13	—	= 100.80
5.	63.00	18.40	—	3.96	0.10	5.36	3.71	2.36	4.22	0.36	—	= 101.47
6.	59.87	22.52	0.32	2.52	0.13	2.50	0.46	4.42	5.78	2.24	0.30 ⁽¹⁾	= 101.06
7.	73.39	14.12	0.77	0.67	—	1.25	0.29	4.47	3.66	1.22	—	= 99.94
8.	61.44	17.08	3.67	2.42	—	6.21	1.14	3.86	4.06	2.04	—	= 101.92
9.	61.54	15.97	1.93	2.98	—	5.52	0.82	4.55	4.48	1.39	2.43	= 101.61
10.	64.66	20.03	—	—	—	1.21	—	8.61	5.44	—	—	= 99.95
11.	57.01	20.81	4.13	—	—	2.91	1.23	6.30	5.92	1.41 ⁽²⁾	—	= 99.72
12.	55.11	20.90	6.11	—	—	3.54	1.21	7.52	5.31	1.04 ⁽²⁾	—	= 100.74
13.	66.46	12.50	10.11	0.78	—	1.25	0.30	1.68	1.99	5.05 ⁽²⁾	—	= 100.13
14.	81.67	9.15	1.72	—	—	0.78	—	4.83	2.38	0.31 ⁽²⁾	—	= 100.84
15.	77.74	9.45	2.23	—	—	1.94	0.66	4.08	3.66	1.19	—	= 100.95
16.	67.31	8.91	2.17	3.58	—	5.13	1.44	—	6.30	1.60	—	= 100.44

(¹) P²O⁵. (²) Loss on ignition. In 12 and 13, traces of Mn and P²O⁵.

S. de Luca (*Compt. rend.* lxxxvii. 174) has detected lithium in the waters and certain earthy decomposition-products of the trachytic rocks of the Solfatara of Puzzuoli.

On the Classification of Trachytes, see Dölter (*Verh. geol. Reichsanst.* 1873, 172) and Szabo (*ibid.* 310). On the Trachytes of the Visegrad range near Budapest, see A. Koch (*Zeitschr. géol. Ges.* xxviii. 293; *Jahresb. f. Chem.* 1876, 1289).

TRAP-ROCKS. The trap-rocks of Connecticut consist, according to G. W. Hawes (*Sill. Am. J.* [3], ix. 185), partly of diabases, partly of chloritic dolerites. The latter are metamorphosed dolerites, but the alteration has been produced, not by contact with the atmosphere (as in that case they would contain no ferrous oxide) but at the moment of eruption, by assumption of subterranean water and carbonic acid. For analyses, see the paper above cited; also *Chem. Soc. J.* xxix. 350; *Jahresb. f. Chem.* 1875, 1272).

On *Trap-granulite*. See GRANULITE (vii. 578).

TRAUTWEINITE. This name is applied by E. Goldsmith (*Sill. Am. J.* [3], v. 313) to microscopically small hexagonal crystals, implanted on chrome-iron ore from California. Qualitative analysis showed the presence of chromium, iron, and manganese.

TREHALOSE or **MYCOSE**, C¹²H²²O¹¹ (iii. 1068). On the occurrence of this kind of sugar, together with glucose and mannitol, in the higher kinds of fungi, see MANNITOL (p. 1267).

TREMOLITE. This mineral has been found in veins in the granular limestone, to the east of Friedberg, in Austrian Silesia (Neminar, *Min. Mitth.* 1875, 111).

2040 TRIACETYL-EMODIN—TRIAZO-COMPOUND, $C^{36}H^{39}N^5$.

TRIACETONALAMINE, $C^6H^{10}NO$, and **TRIACETONAMINE**, $C^6H^{11}NO$. See ACETONAMINES (pp. 29, 32).

TRIACETYL-ANTHRAPURPURIN, $C^{20}H^{14}O^8 = C^{14}H^5(C^2H^3O)^3O^3$. See ANTHRAPURPURIN (vii. 89).

TRIACETYL-EMODIN, $C^{15}H^7(C^2H^3O)^3O^3$. Emodin (p. 732) treated with glacial acetic acid yields, according to the temperature, mono- or tri-acetyl-emodin. The former crystallises from glacial acetic acid in golden-yellow laminae melting at about 180° ; the latter in light yellow needles melting at 190° . Both are easily reconverted into emodin by heating with alkalis (Liebermann, *Ber.* viii. 970).

TRI- and DI-ACETYL-FLAVOPURPURIN. The diacetyl-derivative, $C^{14}H^9(C^2H^3O)^2O^3$, is the chief product obtained by boiling flavopurpurin (p. 111) with acetic anhydride. When recrystallised from glacial acetic acid, it forms golden-yellow laminae, very slightly soluble in that liquid, still less soluble in alcohol. It sublimes at 125° , melts at 238° , and is readily decomposed by potash, sodium carbonate, and ammonia.

Triacetyl-flavopurpurin is found in the mother-liquors of the diacetyl-compound, and may be formed from the latter or from flavopurpurin by heating acetic anhydride at 180° – 200° . From glacial acetic acid, in which it is much more soluble than the diacetyl-compound, it crystallises in sulphur-yellow needles, which melt at 195° – 196° , and are decomposed by potash or by sodium carbonate only at the boiling heat.

TRIACETYL-HYDROCYANROSAURIN, and **TRIACETYL-LEUCOROSAUURIN**. See ROSAUURIN (p. 1762).

TRIACETYL-PURPURIN, $C^{14}H^5(C^2H^3O)^3O^3$. See PURPURIN (p. 111).

TRIACETYL-TRIISOXYLENE, $C^{14}H^{16}O^8 = C^6H(CH^3)^2(O.C^2H^3O)^2$. See XYLOQUINONES.

TRIAMIDOBENZENE, $C^6H^3N^3 = C^6H^3(NH^2)^3$ [1 : 1 : 5]. This compound, originally obtained by the dry distillation of triamidobenzoic acid (vii. 147), is also produced by the reduction of dinitraniline with tin and hydrochloric acid. It is most readily separated from the resulting hydrochloride by distillation with lime from short combustion-tubes bent downwards. The product thus formed is however not so pure as that which is obtained from triamidobenzoic acid, the former boiling at 340° , whereas the latter boils at 330° , though the two are theoretically identical (H. Salkowski, *Ber.* vi. 139). By oxidation it yields a colouring matter, which is also formed by heating chrysoidine with dilute hydrochloric acid at 150° – 160° (Hofmann, *Ber.* x. 213).

Acetyl-ethenyl-triamidobenzene, $C^{10}H^{11}N^3 = C^6H^3(NH.C^2H^3O)(N^2H.C^2H^3)^2$, formed by heating triamidobenzene with twice its weight of glacial acetic acid for ten hours, then adding water and evaporating down, crystallises with $2H^2O$ in geodes of prismatic crystals; melts at 85° – 90° ; gives off its water, and resolidifies at 100° ; dissolves readily in hot water, very sparingly in cold water. The anhydrous compound when distilled gives off a small quantity of acetic acid; its boiling point is above that of mercury.

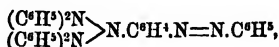
Acetyl-ethenyl-triamidobenzene is converted by hydrochloric acid, with separation of acetic acid, into *ethenyl-triamidobenzene hydrochloride*, $C^6H^3(NH^2)(N^2H.C^2H^3).2HCl + 1\frac{1}{2}H^2O$, which forms easily soluble, highly lustrous crystals, mostly having a faint reddish colour and apparently belonging to the triclinic system. At 100° they give off their water and part of the hydrochloric acid (H. Salkowski a. C. Rudolph, *Ber.* x. 1692).

TRIAMIDOPHENOL, $C^6H^2(NH^2)^3OH$. On the action of bromine and water on this compound, see PHENOLS (p. 1523).

TRIAMYL-PHOSPHINE, $(C^3H^{11})^3P$. See PHOSPHINES (vii. 955).

TRIAZO-COMPOUND, $C^{36}H^{20}N^5$. Aniline and diphenyl-nitrosamine act strongly on one another, forming water, diazo-amidobenzene, amidazobenzene, diphenylamine, and the compound $C^{36}H^{20}N^5$, which is sparingly soluble in alcohol, and crystallises from aniline in flat, ruby-coloured, shining needles, melting at 236° . It is best prepared by heating 10 pts. diphenylnitrosamine, 10 aniline hydrochloride, and 200 dry aniline for an hour and a half at 120° – 125° , mixing the product cooled to 60° with an equal volume of alcohol, washing the crystals which separate with alcohol,

drying them, and recrystallising from a ten-fold quantity of aniline. The body thus obtained has probably the constitution



and may be called a triazo-compound, as it contains 3 atoms of nitrogen linked together. It dissolves in strong sulphuric acid with violet coloration, and turns violet without dissolving when heated with hydrochloric acid. It is also formed when 10 pts. amidazobenzene, 10 diphenylamine, 10 aniline hydrochloride, and 200 aniline are treated as above (O. N. Witt, *Ber.* x. 1309).

TRIBENZHYDROXYLAMINE, $\text{N}(\text{C}^6\text{H}^5\text{O})^3\text{O}$. See HYDROXYLAMINE (p. 1079).

TRIBENZOYL-ANTHRAPURPURIN, $\text{C}^{14}\text{H}^5(\text{C}^6\text{H}^5\text{O})^3\text{O}^3$. See ANTHRAPURPURIN (vii. 90).

TRIBENZOYL-DIAMIDOPHENOL, $\text{C}^6\text{H}^4(\text{OH})^2 < \begin{array}{c} \text{N}(\text{C}^6\text{H}^5\text{O}^2)^2 \\ \text{NH}(\text{C}^6\text{H}^5\text{O}) \end{array}$. See PHENOL (p. 1523).

TRIBENZOYLENE-BENZENE, $\text{C}^{22}\text{H}^{12}\text{O}^3 = \text{C}^6(\text{C}^6\text{H}^4\text{CO})^3$. This appears to be the constitution of the yellow body ($\text{C}^6\text{H}^4\text{O}$), which Gabriel a. Michael obtained by the action of dehydrants on phthalyl-acetic acid (p. 1622). It does not take up either hydrogen or bromine, does not melt at 450° , and is not attacked even by hot potash-ley. Melting potassium hydroxide, however, converts it into phenenyl-tribenzoic acid, $\text{C}^6\text{H}^2(\text{C}^6\text{H}^4.\text{CO}^2\text{H})^3$, which may be purified by separating it from the fused mass, converting it into ammonium salt, exhausting this with alcohol, and repeating these operations several times upon the residue. The phenenyltribenzoic acid may then be separated from the residue by hydrochloric acid, and crystallised from alcohol or glacial acetic acid by mixing the solutions with hot water. Phenenyl-tribenzoic acid thus obtained forms prisms which dissolve easily in alcohol, ether, and glacial acetic acid, sparingly in benzene and carbon sulphide; it melts at 259° – 261° , and undergoes partial carbonisation at 447° . The silver salt contains $\text{C}^{22}\text{H}^5\text{Ag}^3\text{O}^6$ or $\text{C}^{22}\text{H}^5\text{AgO}^3.311\text{H}^2\text{O}$. The acid is not altered by nascent hydrogen, but when distilled over red-hot potassium hydroxide, it yields triphenylbenzene (Gabriel a. Michael, *Ber.* xi. 1007, 1679).

TRIBENZYLAMINE, $\text{N}(\text{CH}^2\text{C}^6\text{H}^5)^3$. The crystalline forms of this base and of some of its salts have been determined by R. Panebianco (*Gazz. chim. ital.* 1878, 854). The base itself and the platinochloride crystallise in the monoclinic system; the hydrochloride in the hexagonal system. The sulphate forms colourless monoclinic crystals, insoluble in water and in ether, soluble in alcohol, and melting with incipient decomposition at 106° – 107° . *Tribenzylamine-alum*, $\text{Al}(\text{C}^6\text{H}^5)^3\text{NH}(\text{SO}^2)^2.12\text{H}^2\text{O}$, crystallises in cubo-octohedrons, with octohedral cleavage; it is soluble in water, insoluble in alcohol and ether, melts in its water of crystallisation at about 110° , and decomposes at about 120° . *Tribenzylamine nitrate*, $(\text{C}^6\text{H}^5)^3\text{N}.\text{HNO}^3$, crystallises in the orthorhombic system, is slightly soluble in water and in alcohol, insoluble in ether, and melts with decomposition at 120° .

Tribenzylamine, subjected to exhaustive chlorination in presence of iodine, is converted into perchlorobenzene and perchloromethane (Ruoff, *Ber.* ix. 1483). Heated in a salt-water bath with *ethyl iodide*, it yields a crystallised iodide which dissolves in alcohol, melts at 190° , and is resolved into its components by the action of silver oxide (G. Vasca-Lanza, *Ber.* vii. 82).

TRIBROMACETAMIDE, $\text{NH}^2.\text{C}^2\text{Br}^2\text{O}$, is formed, together with dibromacetamide and other brominated products, by the action of bromine on asparagine suspended in water. The action is very energetic, and on exhausting the resulting red liquid with ether, leaving the ether to evaporate, placing the residue over sulphuric acid till it solidifies, and recrystallising it from water, tribromacetamide separates out first, while dibromacetamide (melting at 156° – 157° , resolidifying at about 125°) crystallises from the mother-liquors after neutralisation with ammonia (Guareschi, *Gazz. chim. ital.* 1876, 375). Tribromacetamide is also formed by the action of ammonia on hexbromacetone (Weidel a. Grüber, p. 1524).

Tribromacetamide crystallises in shining white lamellæ, which melt at 119.5° – 121° , and are reproduced at 96° . It dissolves sparingly in alcohol, ether, and cold water, and is resolved by boiling with alkalis into bromoform, carbon dioxide and ammonia (Guareschi). Sulphuric acid converts it into ammonium sulphate and tribromoacetic acid (Weidel a. Grüber).

TRIBROMACETANILIDE, $\text{C}^6\text{H}^2\text{Br}^3.\text{NH}(\text{C}^6\text{H}^5\text{O})$. See ACETAMIDES (BROMOPHENYL-), p. 5.

TRIBROMACETIC ACID, CBr_3COOH (p. 18). This acid is formed, together with ammonium sulphate, by heating tribromacetamide for several hours in a reflux apparatus at 128° – 130° , with a mixture of 3 pts. sulphuric acid and 2 pts. water (Weidel & Gruber, *loc. cit.*); also, together with dibromacetic acid (which remains in the mother-liquors), by the action of bromine on a strong solution of malonic acid (Petrieff, *Ber.* viii. 355).

Ethyl Tribromacetate, $\text{CBr}_3\text{COOC}^2\text{H}_5$, is formed by heating the dibromacetic ether with 1 mol. bromine at 120° . When freed from absorbed hydrogen bromide by heating in a stream of carbon dioxide, it forms an oily liquid which fumes strongly in the air and decomposes partly when distilled. It is decomposed by water and alcohol, the products of decomposition containing bodies which reduce an ammoniacal silver solution (Kessel, *Ber.* xi. 1917).

TRIBROMACETOPHENONE-*o*-CARBOXYLIC ACID, $\text{CBr}_3\text{CO}\cdot\text{C}^6\text{H}_4\cdot\text{CO}^2\text{H}$. See PHENYL-KETONES (p. 1565).

TRIBROMALOÏN, $\text{C}^6\text{H}^3\text{Br}^3\text{O}^2$, is formed, together with small quantities of more or less highly brominated products, by the action of bromine-water on barbaloin (p. 63). It crystallises in yellow needles (E. Schmidt, *Arch. Pharm.* [3], viii. 496).

TRIBROMAMIDOBENZENESULPHONIC ACID. See BENZENESULPHONIC ACIDS (p. 233).

TRIBROMAMIDOBENZOIC ACID, $\text{C}^6\text{H}(\text{NH}^2)\text{Br}_3\text{CO}^2\text{H}$ [$\text{CO}^2\text{H} : \text{NH}^2 = 1 : 3$], is formed by the action of bromine on metamidobenzoic acid, and yields a tribromobenzoic acid melting at $186\cdot5^\circ$ (H. Vollbrecht, *Ber.* x. 1904).

TRIBROMANHYDROPYRURIL, $\text{C}^8\text{H}^3\text{Br}^3\text{N}^4\text{O}^2$. See PYRACEMIC UREIDES (p. 1721).

TRIBROMANTHRAQUINONE, $\text{C}^{14}\text{H}^3\text{Br}^3\text{O}^2$. One modification of this compound is obtained by heating anthraquinone with bromine containing iodine to 275° . When purified by boiling it with soda-ley, and crystallising the residue from glacial acetic acid, it forms needles having a faint yellow colour, melting at 186° , and subliming at a higher temperature. It dissolves readily in toluene, nitrobenzene, chloroform, carbon sulphide, and ligroin. Strong sulphuric acid dissolves it without decomposition. Heated with bromine at 320° , it is converted into a tetrabromanthraquinone, which, after purification as above, crystallises in yellow scales melting at 295° – 300° . The tribromo-compound (1 pt.) is converted by heating with sodium hydroxide (2 pts.) at 200° – 210° into purpurin; with potassium hydroxide at a lower temperature into hydroxypurpurin, $\text{C}^{14}\text{H}^6\text{O}^6$ (Diehl, *Ber.* xi. 179, 183).

Another modification of tribromanthraquinone is formed by oxidising pentabromanthracene with chromic acid dissolved in glacial acetic acid. This product melts at 365° , sublimes in broad flat needles, dissolves with moderate facility in the homologues of benzene and in glacial acetic acid, only sparingly in carbon sulphide, chloroform, and benzene, and is nearly insoluble in alcohol and in ether (Hammer-schlag, *Ber.* x. 1212).

TRIBROMETHANE, $\text{C}^1\text{H}^3\text{Br}^3$. The α -modification, CH_3CBr_3 (b. p. 187° – 188°), appears to be formed, together with α -dibromethane, CH_3CHBr_2 (b. p. 109° – 110°), by the action of bromine on ethyl bromide (Denzel, *Ber.* xi. 1739).

TRIBROMETHYLENE, C^2HBr_3 . On the formation of the liquid and solid modifications of this compound from acetylene tetrabromide, see ACETYLENE (p. 35). Liquid tribromomethylene, agitated with oxygen gas, is converted into dibromacetyl bromide, $\text{C}^2\text{HBr}_2\text{O}\cdot\text{Br}$ (Demole, *Compt. rend.* lxxxvi. 542).

Tribromomethylene Dibromide, $\text{C}^2\text{HBr}_3\text{Br}_2$, is one of the compounds formed by heating mucobromic acid with bromine and water in sealed tubes, its formation being especially abundant when the two substances act on one another in molecular proportion. It crystallises in long colourless needles melting at 50° – 52° , and is converted by alcoholic potash into tetrabromomethylene, C^2Br_4 , melting at 50° (*Liebig's Annalen*, clxv. 297).

TRIBROMETHYL-PHTHALIMIDE. See PHTHALIMIDE (p. 1619).

TRIBROMHYDROCOTARNINE HYDROBROMIDE, $\text{C}^{12}\text{H}^{12}\text{Br}^3\text{NO}^3\cdot\text{HBr}$. See NARCOTINE, OXIDATION-PRODUCTS OF (p. 1382).

TRIBROMOBAPHINITONE, $\text{C}^{26}\text{H}^{23}\text{Br}^3\text{O}^6$. See BAPHINITONE (p. 141).

TRIBROMOBENZENES, $\text{C}^6\text{H}^3\text{Br}^3$. See BENZENES (BROMO-), (pp. 166–169).

TRIBROMOBENZENESULPHONIC ACIDS, $C^6H^2Br^3.SO^3H$. See BENZENESULPHONIC ACIDS (pp. 240-243).

TRIBROMOBENZOIC ACIDS, $C^6H^2Br^3.COOH$. A tribromobenzoic acid, melting at 234° - 235° , was obtained by Reinecke by heating benzoic acid with bromine and water (vi. 310). Another, melting at 186.5° , is produced by the action of nitrous acid and alcohol on the tribromamidobenzoic acid which is obtained by treating metamidobenzoic acid with bromine. This tribromobenzoic acid is sparingly soluble in water and crystallises in needles. Its barium salt forms tabular crystals containing $5\frac{1}{2}$ mol. H^2O (H. Vollbrecht, *Ber.* x. 1704).

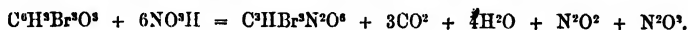
TRIBROMOBILIRUBIN, $C^{32}H^{33}Br^3N^4O^6$ (Maly). See BILIRUBIN (p. 325).

TRIBROMODIACETANILIDE, $C^8H^2Br^3.N(C^2H^3O)^2$. See ACETAMIDES (p. 5).

TRIBROMODIMETHYLETHYLBENZENE, $C^6Br^3(CH^3)^2(C^2H^3)$. See MESITYLENE, HOMOLOGUES OF (p. 1285).

TRIBROMODINITRODIPHENYLAMINE, $C^{12}H^6Br^3(NO^2)^2N$. See PHENYLAMINES (p. 1550).

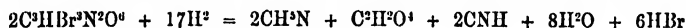
TRIBROMODINITROPROPIONIC ACID, $CBBr^3.C(NO^2)^2.COOH$, is produced by the action of strong nitric acid on tribromophloroglucol:



It forms white, scaly, inodorous crystals having a fine silky lustre, insoluble in cold water and in acids, easily soluble in alcohol and ether. When a few drops of water are added to its recently prepared alcoholic solution, it separates in stellate groups of slender needles. When boiled with water it yields oxalic acid and bromopierin:



By sodium-amalgam it is resolved into methylamine, oxalic acid, and hydrocyanic acid:



(R. Benedikt, *Liebig's Annalen*, clxxiv. 255).

TRIBROMOFLAVOPURPURIN, $C^{14}H^2Br^3O^2(OH)^2$, is formed by adding bromine to a solution of flavopurpurin (p. 111) in glacial acetic acid, and separates in orange-yellow needles melting with decomposition at 284° , sparingly soluble in glacial acetic acid, and dissolving, with yellow-red colour, in soda-ley (Schunck a. Roemer, *Ber.* x. 1225).

TRIBROMOFLUORENE, $C^{12}H^7Br^3$. See FLUORENE (p. 673).

TRIBROMOGLYOXALINE, $C^8HBr^3N^2$. See GLYOXALINE (p. 890).

TRIBROMOGUANAMIDINE, $C^4N^3H^4Br^3O^3$. See GUANAMIDE (p. 900).

TRIBROMOLACTIC ACID, $C^3H^3Br^3O^3$, is formed by prolonged digestion of bromal hydrocyanide, $C^3HBr^3O.HCN$, with dilute hydrochloric acid (Pinner, *Ber.* vii. 1499).

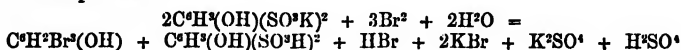
TRIBROMOMETHYL-DIPHENYLAMINE, $C^{14}H^{10}Br^3N$, is formed, together with tetrabromomethyl-diphenylamine and tetrabromodiphenylamine, by the action of bromine on methyldiphenylamine (p. 1550) dissolved in glacial acetic acid. On treating the resulting crystalline pulp with alcohol, the two brominated methyldiphenylamines are dissolved out, while tetrabromodiphenylamine remains in the residue. Tribromomethyl-diphenylamine forms colourless transparent needles insoluble in water, easily soluble in alcohol and in benzene. Fuming nitric acid converts it into tetranitrodibromodiphenylamine, which crystallises from glacial acetic acid in yellow nacreous laminae or rhombohedral tables, but does not appear to have been obtained pure (R. Gnehm, *Ber.* viii. 1040).

TRIBROMONAPHTHALENE, $C^{10}H^3Br^3$. See NAPHTHALENE-DERIVATIVES (p. 1351).

TRIBROMONITROBENZENESULPHONIC ACIDS, $C^6HBr^3(NO^2)SO^3H$. See BENZENESULPHONIC ACIDS (p. 247).

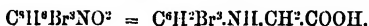
TRIBROMOPHENANTHRENE, $C^{14}H^7Br^3$ (p. 1514).

TRIBROMOPHENOL, $C^6H^3Br^3O$, is formed, together with free phenol-disulphonic acid and other products, by the action of bromine in excess on potassium phenol-disulphonate:



(M. v. Schmidt, *Ber.* xi. 852). It is also formed, together with tribromoresorcinol, by the action of pentabromoresorcinol on aniline (Benedikt, *Ber.* xi. 1559). On its reactions, see PHENOLS (p. 1525).

TRIBROMOPHENYL-GLYCOCINE,



is obtained on adding bromine water to an aqueous solution of phenyl-glycocine (p. 1563) till a permanent coloration is produced, as a white precipitate, insoluble in water, acids, and alkalis, easily soluble in hot alcohol, from which, however, it does not crystallise. From hot glacial acetic acid it crystallises in colourless microscopic needles (Schwobel, *Ber.* xi. 1131).

TRIBROMOPHYLOGLUCOL, $C^6H^3Br^3O^2$. On the conversion of this compound into tribromodinitropropionic acid, see p. 1571.

TRIBROMOPROPIONIC ACID, $C^3H^3Br^3O^2$. An acid of this composition is obtained, together with a large quantity of oxalic acid, by the action of nitric acid in excess on acrolein bromide. It crystallises from boiling benzene, and melts at 93° (Linnemann a. Paul, *Ber.* viii. 1097).

TRIBROMOPYROGALLOL, $C^6Br^3(OH)^3$. See PYROGALLOL (p. 1709).

TRIBROMOQUINONE, $C^6HBr^3O^2$, is formed, together with tetrabromoquinone (bromanil) and other brominated derivatives of quinone, by acidulating an alkaline solution of ethylic succinyl-succinate (see APPENDIX) with sulphuric acid, and mixing it with excess of bromine (F. Herrmann, *Ber.* x. 107).

TRIBROMOPYRORACEMIC ACID, $CBBr^3.CO.CO^2H$. See PYRORACEMIC ACID (p. 1718).

TRIBROMORESORCINOL, $C^6H^3Br^3O^2$, is formed by the action of bromine on an aqueous solution of resorcinoldisulphonic acid, the sulpho-groups being oxidised to sulphuric acid and thereby removed. It crystallises in colourless needles having a silky lustre.

TRIBROMOSTRUTHIN, $C^{14}H^{14}Br^3O^2$. See OSTRUTHIN (p. 1449).

TRIBROMOTOLUENES, $C^6H^2Br^3.CH^3$. See TOLUENE (p. 1990).

TRIBROMO-*p*-TOLUENESULPHONIC ACID, $C^6HBr^3(CH^3)(SO^2H)$. See TOLUENESULPHONIC ACIDS (p. 2012).

TRIBROMOTOLUIDINE, $C^6HBr^3(NH^2)(CH^3)$. See TOLUENES, BROMAMIDO- (p. 1998).

TRIBROMOXYLENES, $C^6HBr^3(CH^3)^2$. See XYLENES.

TRIBUTYLAMINE (normal), $[CH^2(CH^2)^2]^3N$ (b. p. 211° – 215°). See BUTYLAMINES (vii. 222).

TRIBUTYL(ISO)ARSINE. A red crystalline compound of tri-isobutylarsine with arsenic iodide is formed by heating isobutyl iodide with powdered arsenic at 175° – 180° (Cahours, *Compt. rend.* lxxvii. 1403).

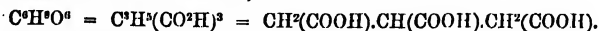
TRIBUTYLENE (ISO), $C^{12}H^{24}$. This hydrocarbon is obtained, together with isodibutylene (p. 1128) by saturating trimethyl-carbinyl iodide with isobutylene, and heating the liquid with calcium oxide at 100° in a sealed tube for three hours. The product, after being freed from lime by digestion with dilute hydrochloric acid, is distilled in a current of steam; and the oily distillate is freed from remaining traces of the iodide by digestion for a few hours with moist silver oxide, then washed, dried, and rectified over an alloy of sodium and potassium. The liquid thus obtained may be separated by fractional distillation into isodibutylene boiling at 102° – 105° , and isodibutylene, boiling at 177° – 178° . The same isodibutylene is obtained by the action of trimethylcarbinyl iodide on isodibutylene in presence of calcium oxide in sealed tubes at 100° (Julie Lermontoff, *Ber.* xi. 1255).

Tri-isobutylene appears also to be contained in the oily condensation-products formed in the preparation of trimethylcarbinol.

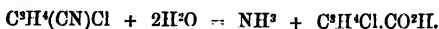
TRIBUTYL(ISO)PHOSPHINE. See PHOSPHINES (vii. 955).

TRIBUTYLSULPHINE-COMPOUNDS. See SULPHINES (p. 1850).

TRICARBALLYLIC ACID,



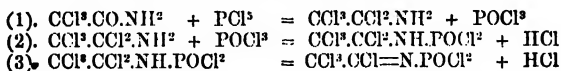
This acid, originally obtained by the action of potash on allyl tricyanide, $\text{CH}^2(\text{CN}).\text{CH}(\text{CN}).\text{CH}^2(\text{CN})$ (v. 879) is also produced: *a.* Together with hydroxy-crotonic acid, $\text{C}^3\text{H}^3\text{O}^3$, by the action of a boiling slightly alkaline solution of potassium cyanide on dichloroglycide, $\text{C}^3\text{H}^3\text{Cl}^2$. Claus a. Kölver, who discovered this reaction (*Ber.* v. 358; *Liebig's Annalen*, clxx. 131), explain it by supposing that a cyanochloroglycide is first formed and then converted in the slightly alkaline solution, with evolution of ammonia, into chlorocrotonic acid:



This acid then decomposes a further quantity of potassium cyanide, forming hydrogen cyanide, which is added on; at the same time the second chlorine-atom is replaced by cyanogen, and both the cyanogen-groups thus introduced are converted into carboxyl-groups, the final product being tricarballylic acid. *β.* Together with a bibasic acid, by the action of potassium cyanide on ethylic monochlorocrotonate (Claus, *Ber.* ix. 223). *γ.* Ethylic acetosuccinate is converted by the action of sodium into ethylic acetotricarballylate, $\text{CH}^2.\text{CO}.\text{C}(\text{CH}^2.\text{COOC}^2\text{H}^3)^2.\text{COOC}^2\text{H}^3$, and this compound saponified by alcoholic potash or baryta-water yields tricarballylic acid (G. Miehe, *Liebig's Annalen*, xc. 322). *4.* Tricarballylic acid appears to be one of the products formed by the action of chlorine on gallic acid (Schreder, *ibid.* clxxvii. 282). *δ.* Tricarballylic acid has been found in a precipitate formed during the evaporation of the juice of very unripe beet; the juice of ripe beet does not yield it (v. Lippmann, *Ber.* xi. 707).

TRICHLORACETAL, $(\text{C}^2\text{H}^2\text{Cl}^2\text{O})^2 = \text{C}^2\text{H}^2\text{Cl}^2(\text{O})(\text{C}^2\text{H}^2)^2$, is formed, together with mono- and dichloroacetal, by the action of chlorine at various temperatures on alcohol of 50 to 75 per cent. It is described by Paternò (vi. 4) and by Krey (viii. 1) as crystallising in colourless needles melting at 72°, and boiling with slight decomposition at 230° (Paternò), melting at 83°, and beginning to decompose at 190° (Krey). H. Byasson, on the other hand (*Compt. rend.* lxxxvii. 26), describes it as a mobile liquid having a density of 1.288, and boiling at 197°. This product probably contained mono- and dichloroacetal.

TRICHLORACETAMIDE, $\text{NH}^2.\text{C}^2\text{Cl}^2\text{O}$. This compound, heated with phosphorus pentachloride, yields tetrachlorethylidene-imidochlorophosphenyl, $\text{C}^2\text{Cl}^2\text{ONP}$, which appears to be formed by the following series of reactions:



Tetrachlorethylidene-imidochlorophosphenyl distils at 255°–259°, and solidifies at 70°–80° to a crystalline mass. Its vapours strongly irritate the eyes and mucous membranes. It is very unstable, and cannot be kept without change; its decomposition yields, amongst other products, trichloroacetonitril (Wallach, *Ber.* viii. 299).

TRICHLORACETANILIDE, or **TRICHLOROPHENYLACET-AMIDE,** $\text{C}^6\text{H}^3\text{Cl}^3.\text{NH}^2.\text{C}^2\text{H}^2\text{O}$, is formed, together with *dichloroacetanilide*, by passing dry chlorine into a solution of 1 pt. acetanilide in 4 pts. acetic acid of 90 per cent. till the weight of the liquid is increased to the amount of 1.05 per cent. It crystallises in needles melting at 204°, dissolves sparingly in ether, carbon sulphide, and ligroin, more readily in alcohol and acetic acid (Beilstein a. Kurbatow, *Ber.* viii. 455). The metameric compound, *Phenyl-trichloroacetamide*, $\text{C}^6\text{H}^5.\text{NH}^2.\text{C}^2\text{Cl}^2\text{O}$, which Tommasi a. Meldola obtained by pouring aniline into trichloroacetyl chloride, crystallises in rhomboidal plates, melts at 94°, and is extremely soluble in ether and in carbon sulphide (p. 6).

TRICHLORACETIC ACID, $\text{CCl}^3.\text{COOH}$. See ACETIC ACID (p. 19). *Potassium trichloroacetate*, heated with bromine in closed vessels at 110°–120°, is converted into potassium bromide, carbon dioxide, and bromotrichloromethane, CCl^3Br . Chlorine acts much less strongly, and only on addition of iodine, producing in the first instance hexchloroethane, C^2Cl^6 (van't Hoff, *Ber.* x. 678).

Ethylic Trichloroacetate is decomposed by potassium cyanide in alcoholic solution, yielding, if water is present, potassium chloride, carbon dioxide, ammonia, and acetic acid; and, if water is absent, carbon dioxide and chloroform (Claus, *Liebig's Annalen*, xcxi. 58). A trichlorinated acetic ether, probably $\text{CH}^3.\text{COO}.\text{CHCl}.\text{CHCl}^2$, is formed by

the action of chlorine at 120° in presence of iodine on ethylidene acetochloride, $\text{CH}^3\text{.CH} < \begin{smallmatrix} \text{Cl} \\ \text{OC}^2\text{H}^3\text{O} \end{smallmatrix}$ (Kessel, *Ber.* x. 1894).

Trichloroacetic Anhydride, $(\text{C}^2\text{Cl}^3\text{O})^2\text{O}$, is formed by the action of trichloroacetyl chloride on trichloroacetic acid (Anschütz, *Ber.* x. 325); also by heating trichloroacetic acid for two days with excess of phosphorus trichloride. It is a colourless liquid, which has a faint odour, boils at 222° – 224° , rapidly absorbs moisture from the air, and is thereby decomposed (Buckney a. Thomsen, *Ber.* x. 698).

TRICHLORACETONE, $\text{CCl}^3\text{.CO.CH}^3$. This compound is obtained by direct chlorination of acetone (p. 26), and, together with other products, by the action of chlorine on the sodium salt of citraconic acid (p. 314).

TRICHLORACETONIC ACID, $\begin{smallmatrix} \text{CH}^3 \\ \text{CCl}^3 \end{smallmatrix} > \text{COH.COOH}$, formed by the action of strong hydrochloric acid at the heat of the water-bath on trichloroacetone-cyanhydrin (p. 26), is a syrupy liquid which is easily decomposed by alkalis, and does not form definite salts (C. Bischoff, *Ber.* viii. 1329).

TRICHLORACETONITRIL, $\text{CCl}^3\text{.CN}$ (p. 33), is decomposed by boiling with milk of lime and more completely by potash, yielding carbon dioxide and chloroform (Beckurts a. Otto, *Ber.* ix. 1591).

TRICHLORACETOPHENONE-ORTHO-CARBOXYLIC ACID, $\text{COCl}^3\text{.C}^6\text{H}^4\text{.COOH}$, is formed by the action of chlorine on phthalylacetic acid suspended in glacial acetic acid (p. 1621).

TRICHLORACETYL BROMIDE, $\text{CCl}^3\text{.CO.Br}$ (b. p. 143°). See ACETYL BROMIDE (p. 21).

TRICHLORACETYL CARBAMIDE, $\text{NH}^2\text{.CO.NH.C}^2\text{Cl}^3\text{O}$, is formed by heating trichloroacetyl chloride with urea (Tommasi a. Meldola, p. 392), also by heating the trichloroacetate of urea with phosphorus pentachloride (Clermont, *Compt. rend.* lxxviii. 848). According to Tommasi a. Meldola, it crystallises from alcohol in needles melting at 150° ; according to Clermont in micaceous laminae, subliming for the most part without decomposition, insoluble in cold, and only slightly soluble in hot water.

TRICHLORACETYL CHLORIDE, $\text{CCl}^3\text{.CO.Cl}$, originally obtained by the action of trichloride or pentachloride of phosphorus on trichloroacetic acid, or of the pentachloride on acetyl chloride (vi. 22; vii. 19), is also formed by the action of chlorine in sunshine on paradichloraldehyde dissolved in carbon tetrachloride (viii. 54); and, according to Friederici (*Ber.* xi. 1970), by passing dry hydrogen chloride over a heated mixture of trichloroacetic acid and phosphorus pentoxide. It boils at 118° . By the action of *phosphine* (PH^3) it is converted into trichloroacetyl phosphide, $\text{C}^2\text{Cl}^3\text{O.PH}^2$ (Steiner, *Ber.* viii. 1178). With *trichloroacetic acid*, it forms the anhydride, $\text{C}^2\text{Cl}^3\text{O.O.C}^2\text{Cl}^3\text{O}$ (Anschütz, *Ber.* x. 1881).

TRICHLORAL HYDROCYANIDE, $\text{C}^6\text{H}^4\text{Cl}^3\text{NO}^3$ (Cech, *Ber.* ix. 1020). This compound, called by Cech *trichloral cyanide*, is formed on mixing a saturated solution of chloral hydrate with a very small quantity of a concentrated solution of potassium cyanide. Crystalline spangles then separate after some time, and on subsequently adding an excess of water, a bulky white precipitate is formed, consisting of microscopic needles, and containing the elements of 3 mol. chloral and 1 mol. hydrogen cyanide, $3\text{C}^2\text{HCl}^3\text{O} + \text{HCN} = \text{C}^6\text{H}^4\text{Cl}^3\text{NO}^3$. This compound is insoluble in water (though extremely hygroscopic), but dissolves in alcohol and benzene, very easily in ether, and crystallises from the last two solvents in white prisms melting at 123° ; from the alcoholic solution it separates in nodules. When heated a few degrees above its melting point, it partly sublimes undecomposed, and when subjected to dry distillation, it yields a sublimate of chloralide, leaving an abundant carbonaceous residue. It is not acted upon by dilute acids in the cold, but when boiled therewith it yields chloral. Heated with soda-lime it gives off ammonia, together with vapours having the odour of 'propane-ethyl.' Heated with *aniline* and potassium cyanide, it gives off hydrogen cyanide, and yields chloral-monoanilide, $\text{CCl}^3(\text{NH.C}^6\text{H}^5)\text{CHO}$.

TRICHLORALALDOLIN, $\text{C}^6\text{H}^4\text{Cl}^3\text{O}^2$, is formed, together with products containing larger and smaller proportions of chlorine, by the action of chlorine on barbaloin (E. Schmidt, *Arch. Pharm.* [3], viii. 496).

TRICHLORANGELACTIC ACID. See TRICHLOROVALEROLACTIC ACID, under BUTYRIC CHLORAL (p. 444).

TRICHLORANILINES, $C^6H^3Cl^3.NH^2$. See pp. 196 and 1549.

TRICHLORANTHRACENE, $C^{14}H^3Cl^3$. When chlorine is passed into a solution of anthracene in chloroform till the viscid mass at first formed becomes thin and transparent, the chloroform then distilled off, and the residual crystalline mass washed with ether and recrystallised from chloroform, dichloranthracene dichloride, $C^{14}H^3Cl^2.Cl^2$, is obtained in transparent colourless prisms melting at $149^\circ-150^\circ$; and on heating this compound to 170° , trichloranthracene is obtained, together with a small quantity of dichloranthracene. The same decomposition takes place gradually when the dichloride is kept in closed vessels. The trichloranthracene thus produced crystallises from alcohol in long yellow needles melting at $162^\circ-163^\circ$, and yielding an alcoholic solution which exhibits a blue fluorescence; it is but slowly attacked by nitric acid. It is perhaps identical with that which Graebe & Liebermann obtained (vii. 90) by the action of phosphorus pentachloride on anthraquinone (F. Schwarzer, *Ber.* x. 376).

TRICHLORANTHRAQUINONE, $C^{14}H^3Cl^3O^2$, is formed by heating anthraquinone with antimony pentachloride in a sealed tube at 180° , and purified by boiling the crude product with hydrochloric acid and crystallising the residue from a mixture of alcohol and benzene. It forms yellow needles, which sublime with decomposition, melt between 284° and 290° , and dissolve in glacial acetic acid, chloroform, and toluene, sparingly also in benzene (Diehl, *Ber.* xi. 179).

TRICHLORETHYLIDENIC ETHERS. See CHLORALIDE (p. 445).

TRICHLORHYDRIN, $C^3H^3Cl^3$. See TRICHLOROPROPANES.

TRICHLORHYDROXYFULMPLATINUM, $Pt^4O^2N^2H^2Cl^3(OH)$. See PLATINUM-COMPOUNDS (p. 1651).

TRICHLOROBENZENES, $C^6H^3Cl^3$. See BENZENE-DERIVATIVES (p. 173).

TRICHLOROBILIRUBIN, $C^{30}H^6Cl^3NO^2$ (Thudichum). See BILE-PIGMENTS (p. 325).

TRICHLOROBUTYLIDENIMIDE, $C^4H^3Cl^3NH$, is formed by heating acetyl-butyl-chloral hydrocyanide, $C^4H^3Cl^3(OC^2H^3O)CN$, for an hour with excess of dry ammonium acetate, and separates gradually on addition of water. It dissolves readily in alcohol, ether, hot benzene, and hot water, less readily in glacial acetic acid, melts at $164^\circ-165^\circ$, and decomposes at 192° , also on exposure to sunshine (Pinner & Klein, *Ber.* xi. 1488).

TRICHLOROCHRYSENE, $C^{18}H^3Cl^3$. See CHRYSENE (p. 464).

TRICHLOROLACTIC ACID, $CCl^3.CHOH.CO^2H$. The ethylic ether of this acid is converted by the action of zinc and hydrochloric acid into ethylic monochloroacrylate, $CHCl=CH.COOC^2H^3$ (Pinner, p. 45). According to W. Rudloff, on the other hand (*Ber.* viii. 434), the chief product of the reduction of ethylic trichlorolactate is ethylic dichlorolactate.

On the Action of Trichlorolactic Acid on Chloralide, see p. 445.

TRICHLOROLACTIC BROMALIDE, $CCl^3.CH<\overset{O}{\underset{COO}{C}}>CH.CBr^2$. On the crystalline form of this compound, see Wallach (*Liebig's Annalen*, cxiii. 1; *Jahresb. f. Chem.* 1878, 690).

TRICHLOROMETHYLSULPHONIC CHLORIDE, $CCl^3.SO^2Cl$, which Kolbe obtained by the action of moist chlorine on carbon disulphide (v. 559), is also produced by the action of water on the chloride, $SO^2Cl.CHCl.COCl$, resulting from the action of phosphorus pentachloride on sulphacetic acid. On treating this chloride with water, the greater part dissolves, and trichloromethylsulphonic chloride remains as a white substance melting at 137° , and agreeing in other respects with the product obtained by Kolbe (R. Siemens, *Ber.* vi. 659).

TRICHLORONAPHTHALENES, $C^{10}H^3Cl^3$. See NAPHTHALENE (p. 1350).

TRICHLOROPHENOL, $C^6OH.Cl.H.Cl.H.Cl$. See PHENOL (p. 1525).

TRICHLORONITROBENZENES, $C^6H^2(NO^2)Cl^3$. The modification $C^6.NO^2.Cl.Cl.H.H.Cl$ is prepared as follows:—The acetyl-derivative of paradichloroanilino, $C^6.NH^2.Cl.H.H.Cl.H$, yields by nitration two dichloronitracetanilides, of which the one least soluble in benzene and melting at $204^\circ-205^\circ$ may be transformed into a dichloronitraniline, $C^6.NH^2.NO^2.Cl.H.H.Cl$, convertible by Griess's reaction into the trichloronitrobenzene, $C^6.Cl.NO^2.Cl.H.H.Cl$, which is identical with that above formulated. This trichloronitrobenzene crystallises from ligroin in colourless needles melting at $86^\circ-89^\circ$, and is converted by reduction and replacement of the amido-

group by chlorine into consecutive tetrachlorobenzene (p. 174), (Beilstein a. Kurbatow, *Liebig's Annalen*, xcii. 228).

The trichloronitrobenzene, $C^6H^3Cl^3NO^2$, obtained from *symmetrical* trichlorobenzene, is converted by heating for several days with alcoholic ammonia at 200° into *chloronitro-m-phenylenediamine*, $C^6H^2NO^2NH^2.H.Cl.H.NH^2$, which when purified by crystallisation from carbon sulphide or ligroin, forms red needles melting at 192° – 194° , easily soluble in alcohol, less soluble in acetic acid of 50 per cent. or in benzene, very sparingly soluble in ligroin (Beilstein a. Kurbatow).

The trichloronitrobenzene melting at 56° , which is formed by nitration of *consecutive* trichlorobenzene (p. 173), is converted by heating with alcoholic ammonia at 210° into a dinitraniline, which melts at 162° – 163° , and may be converted by nitrous ether into ortho-dichloronitrobenzene (p. 187), (Beilstein a. Kurbatow).

TRICHLOROPHENOMALIC ACID. The substance so named by Carius (vi. 917), obtained by the action of chlorous acid on benzene, and supposed to have the composition $C^6H^2Cl^3O^2$, has been shown by Krafft (*Ber.* x. 797) to be identical with trichloroquinol.

TRICHLOROPHENYL-GUANIDINE, $CH^2(C^6H^4Cl)^3N^2$. See GUANIDINE (p. 907).

TRICHLOROPHTHALIC ACID, $C^8HCl^3(COOH)^2$, is formed, together with another compound, probably a quinone, by the action of strong nitric acid on β -pentachloronaphthalene. It is a yellowish-white mass, converted by heat into an anhydride which crystallises in long needles melting at 157° (Atterberg a. Widman, *Ber.* x. 1841).

TRICHLOROPROPANES, $C^3H^3Cl^3$. Three of these compounds are known, viz.:

	B. p.	Sp. gr.
α -Trichloropropane or Trichlorhydrin, $CH^2Cl.CHCl.CH^2Cl$	155°	1.41 at 0°
β -Trichloropropane, $CH^3.CHCl.CHCl^2$	140°	1.402 at 4°
γ -Trichloropropane, $CH^3.CCl^2.CH^2Cl$	123°	1.350 at 0°

Respecting the first, see i. 894; vi. 433; vii. 319. According to Belohoubek (*Ber.* ix. 924), it is formed, together with the γ -modification and other products, by the action of chlorine on propylene (from allyl iodide, glacial acetic acid, and zinc), and may be separated by fractional distillation. It is decomposed by aluminium iodide, with formation of allyl iodide, aluminium chloride, and free iodine (Gustavson, *Ber.* ix. 1607).

β -Trichloropropane is formed by the action of chlorine on propylene chloride in sunshine; also, together with trichlorhydrin and a trace of a tetrachloride, by heating propylene chloride (from allyl iodide) with dry iodine chloride in small portions at 160° , and may be separated by treating the product with potash-ley and with sodium sulphite, washing it with water, drying over calcium chloride, and fractional distillation (Friedel a. Silva, *Compt. rend.* lxxiv. 805).

γ -Trichloropropane, or Monochloromethylchloracetol, is formed by the action of chlorine in sunshine on methylchloracetol, $CH^3.CCl^2.CH^3$ (vii. 1018), also by treating the same compound with iodine chloride. When heated with alcoholic potash at 100° , it yields, together with products which reduce ammoniacal silver solution, an ether which gives a white precipitate with silver solution. When heated with water in sealed tubes, it dissolves more readily than trichlorhydrin, leaving a small quantity of black liquid. The water contained, not glycerol, but a non-volatile body which resinised when the water was evaporated by heat, reduced ammoniacal silver solution, and remained as a yellow amorphous mass when its solution was evaporated in a vacuum. Its analysis gave numbers leading to the formula $CH^3.CO.CHO$. By oxidation with nitric acid it yielded a body having an odour like that of pyroracemic acid. The black residue above mentioned yielded on fractional distillation two dichloropropylenes boiling at 75° and 94° (Friedel a. Silva, *loc. cit.*)

TRICHLORORESORCINOL, $C^6HCl^3(OH)^2$. See RESORCINOL (p. 1749).

TRICHLOROTOLUENES, $C^7H^3Cl^3$. See TOLUENE (p. 1993).

TRICHLOROTOLUQUINOL, $C^7H^3Cl^3O^2$, and **TRICHLOROTOLUQUINONE**, $C^7HCl^3O^2$. See TOLU-QUINOL and -QUINONE (p. 2029).

TRICHLOROVALEROLACTAMIDE, $C^4H^3Cl^3(OH)CONH^2$. See VALERIC ACIDS.

TRICODEINE, $C^{100}H^{126}N^6O^{13}$. This polymeride of codeine is formed by heating codeine with a strong solution of zinc chloride for a short time and at a comparatively

low temperature; by longer heating at higher temperatures a mixture of tricodeine and tetracodeine, $C^{14}H^{16}N^2O^2$, is obtained (Wright, *Chem. Soc. J.* xxvii, 107). See further, vii, 373-375.

TRIDYMITE. On the occurrence of tridymite in volcanic rocks, see H. Möhl (*Jahrb. f. Min.*, 1873, 453; *Jahresb. f. Chem.* 1873, 1150); in the lava of Santorin, Fouqué (*Compt. rend.* lxxxii, 1141; *Jahresb. f. Chem.* 1876, 1291). On twin-formations of tridymite, G. vom Rath (*Pogg. Ann.* clii, 1; *Jahresb. f. Chem.* 1874, 1242).

TRIETHYLAMIDACETOCHLORIDE, $C^2H^5CINO^2 = \begin{array}{c} (C^2H^5)^3N-Cl \\ | \\ CH^2.COOH \end{array}$

is produced by the action of triethylamine on ethyl monochloracetate, and may be separated from triethylamine hydrochloride formed at the same time by boiling with baryta-water. It is not decomposed by strong bases, even at a rather high temperature. When treated with silver oxide it is converted into triethylglycocine (Brühl, *Ber.* viii, 1406).

TRIETHYLAMINE, $(C^2H^5)^3N$. On the formation of this base from dichlor-ethylamine, and its reactions with methylene iodide and ethyl chloropropionate, see ETHYLAMINES (p. 748). By oxidation with permanganate it yields carbonic and acetic acids (Wallach & Claisen, *Ber.* viii, 1237).

TRIETHYLAZONIUM IODIDE, $(C^2H^5)^3N^+H^2.C^2H^5I$ (p. 1061).

TRIETHYLBENZENE, $C^6H^5(C^2H^5)^3$. See MESITYLENE, HOMOLOGUES OF (p. 1285).

TRIETHYLBENZYLAMMONIUM IODIDE, $(C^2H^5)^3N(C^2H^5)I$. See BENZYLAMINES, under TOLUENES (AMIDO-), (p. 2001).

TRIETHYL-DICARBOPIRROLAMIDE, $C^2H^5N^2O^2$, formed, together with other products, by dry distillation of ethylamine mucate, is insoluble in water and melts at $229^\circ-230^\circ$. See PYRROLINE (p. 1728).

TRIETHYLENE-BORIC ETHER, $B(OC^2H^5OH)^3$. See TRIHYDROETHYL BORATE (*infra*).

TRIETHYLENE-TRITOLYLTRIAMINE, $N^3(C^2H^5)^3(C^6H^4.CH^3)^3$, is formed, together with ethylene-ditolylidiamine, by the action of ethylene bromide on toluidine at 150° . The two bases may be separated by means of alcohol, in which the former is very sparingly, the latter freely soluble. The triethylene-base crystallises in very beautiful needles melting at 186° ; its hydrochloride forms needles melting at 189° . *Ethylene-ditolylidiamine*, $N^2(C^2H^5)(C^6H^4.CH^3)^2H^2$, is best purified by separation from its salts. It forms crystals melting at 97.5° . Its hydrochloride is very soluble in water, and crystallises in long white needles (Gretillat, *Monit. scient.* [3], iii, 383).

TRIETHYL-GLYCOCINE, $\begin{array}{c} (C^2H^5)^3N.CH^2 \\ | \quad | \\ O-CO \end{array}$, formed by the action of silver

oxide on triethylamidacetoehloride (*supra*), is a liquid which begins to boil at 210° , and is partly resolved by distillation into triethylamine and carbonaceous products (Brühl, *Ber.* viii, 479).

TRIETHYL-METHYLSTIBINE, $Sb(C^2H^5)^3(CH^3)$. The hydroxide of this radicle (i. 347), which, according to Friedländer, is optically active, has been shown by Le Bel (*Bull. Soc. Chim.* [2], xxvii, 444) not to possess this property when pure.

TRIETHYLNAPETHYLPHOSPHONIUM IODIDE, $P(C^2H^5)^3(C^6H^5)I$, formed by the combination of diethylnaphthylphosphine with ethyl iodide, crystallises from water in colourless laminae melting at 209° .

TRIETHYLPHENYLARSONIUM IODIDE, $As(C^2H^5)^3(C^6H^5)I$. See PHENYL-ARSENIC COMPOUNDS (p. 1554).

TRIETHYLPHENYLPHOSPHONIUM IODIDE, $P(C^2H^5)^3(C^6H^5)I$. See PHOSPHINES (p. 1580).

TRIETHYLPHOSPHINE OXIDE, $P(C^2H^5)^3O$. In connection with the method of preparing this compound given by Carius and by Crafts & Silva (vii, 953), F. A. Emmerton (*Amer. Chem.*, 1873, iv, 9) observes that when 1 mol. phosphorus triiodide is treated with 3 mol. ethyl iodide, free iodine is given off, and a body is formed which, after treatment with solid potash, yields on distillation triethylphosphine oxide.

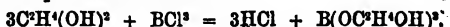
TRIETHYLSSENONIUM COMPOUNDS, $(C^2H^5)^3SeI$, &c. See SELENIUM-COMPOUNDS, ORGANIC (p. 1788).

TRIETHYLSILICOL, $(C^2H^5)_3SiOH$. See SILICON-ETHYL (p. 1794).

TRIETHYLSULPHINE-COMPOUNDS. See SULPHINES (p. 1850).

TRIETHYLTELLURIUM-COMPOUNDS. See TELLURIUM-COMPOUNDS, ORGANIC (p. 1900).

TRIHYDROXYETHYL BORATE, $B(OC^2H^4OH)_3$. *Triethylene-monoboric Ether*.—This compound is formed by treating ethylene alcohol with an excess, first of gaseous and then of liquid boron chloride :



The product crystallised from chloroform is a solid yellowish mass consisting of microcrystalline laminae, nearly insoluble in ether, melting at about 161.7° , and decomposing in moist air (C. Counciler, *Ber.* xi. 1106).

TRI-IODOMETHYL-ROSANILINE. See TRIMETHYL-ROSANILINE (p. 2053).

TRI-IODORESORCINOL, $C^6H^3I^3O^2$. See RESORCINOL (p. 1749).

TRI-ISOBUTYLENE, $C^{12}H^{24}$, appears to be contained in the oily condensation-products formed in the preparation of trimethylcarbinol by treating isobutylene with a mixture of 3 pts. sulphuric acid and 1 pt. water (GoraiNOW a. Butlerow, *Liebig's Annalen*, clxix. 146).

TRIMELLITIC ACID, $C^8H^4(CO^2H)^3$ [1 : 2 : 4]. See MELLITIC ACID (p. 1274). This acid is formed, together with isophthalic acid, by oxidising colophony with dilute nitric acid. 100 g. pulverised colophony and 2 litres of nitric acid (1 vol. commercial acid to 2 vol. water) are introduced into a retort with its beak directed upwards, and the liquid is heated to boiling, whereupon the colophony melts, and is quickly attacked, with copious evolution of red vapours, and converted into an orange-yellow viscid mass. After the boiling has been continued for six or eight hours, fresh resin and strong nitric acid are added alternately, till about 1 kg. resin has been introduced, the contents of the retort being kept in constant ebullition; this process takes about a fortnight. The resulting wine-yellow liquid, which on addition of water should merely show turbidity, and not yield any lumpy precipitate, is then distilled off till the remaining liquid begins to froth; and this liquid, while still hot, is poured into a tenfold volume of cold water, decanted after twenty-four hours from the varnish-like resin which separates, and evaporated to a syrupy consistence. The whole then solidifies after a while to a thick crystalline pulp, which may be freed from the syrupy mother-liquor by means of an aspirator and porous earthenware plates, and afterwards boiled with water. The extract on cooling deposits isophthalic acid in slender needles, and on further concentration, first a little more of the same acid and then trimellitic acid, which may be purified by solution in alcohol and crystallisation from water.

Trimellitic acid thus obtained (about 30 g. from 500 g. colophony) melts at 218° ; its anhydride, obtained by heating it to fusion, melts at 157° . When evaporated down with milk of lime and then heated, it yields benzene. Its air-dried *barium salt* contains $(C^8H^4O^4)^2Ba^2 + 4H^2O$ (comp. vi. 813), and gives off $3H^2O$ at 160° . The *silver salt*, $C^8H^4O^4Ag^3$ (dried at 120°), is a white precipitate, not much altered by exposure to light, soluble in a large quantity of water.

The syrupy mother-liquor of the trimellitic acid did not yield any other crystallised body, but on further treatment with nitric acid it gave a smaller quantity of a crude crystallisation containing a small proportion of trimellitic acid, but consisting mainly of terebic acid (J. Schreder, *Liebig's Annalen*, clxxii. 93).

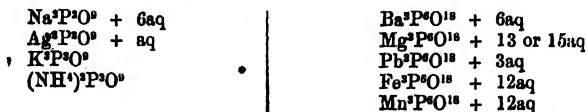
TRIMESIC ACID, $C^8H^4(CO^2H)^3$ [1 : 3 : 5]. The symmetrical disposition of the carboxyl-groups in this acid is shown by its formation by oxidation of mesitylenic acid (vi. 811; viii. 1286); and as it is also produced from the phenol-tricarboxylic acid, $C^6H^3(OH)(CO^2H)^3$, obtained by heating disodic salicylate in a stream of carbon dioxide, by converting this tribasic acid into the chlorinated acid, $C^6H^2Cl(CO^2H)^3$, and reducing the latter with zinc and a dilute acid, it follows that this phenol-tricarboxylic acid must have the constitution of hydroxytrimesic acid, $[OH : CO^2H : CO^2H : CO^2H = 1 : 2 : 4 : 6]$. (See p. 1535.)

Trimesic acid is also formed by oxidation of triethylbenzene with chromic acid (p. 1285), and in very small quantity by fusion of sulphometabromobenzoic acid with sodium formate (p. 295).

TRIMETAPHOSPHORIC ACID, $P^3O^5H^3$, probably = $\begin{matrix} HO \\ \diagup \quad \diagdown \\ OPO.OPOPO.OH \end{matrix}$ (iv.

539). Several salts of this acid have been prepared and analysed by O. G. Lindbom (*Ber.* viii. 122). The *sodium salt* was prepared by heating ordinary sodium-ammonium phosphate in a platinum dish over a gas-lamp, the heat being gradually raised till the

pasty mass became crystalline like sugar, the whole then pulverised and again strongly heated, with stirring, but so as carefully to avoid fusion, which would result in the formation of the insoluble hexphosphate. In this manner, 95 per cent. of the sodium-ammonium phosphate is obtained as sodium trimetaphosphate. The following are the formulæ of the salts examined :



Double Salts :



The weaker bases do not appear to form trimetaphosphates of definite composition. With mercurous nitrate, a basic salt was obtained having the composition $5\text{Hg}^2\text{O}, 3\text{P}^3\text{O}^9$.

TRIMETHOXY-TRIHYDROXYDIPHENYL, or **TRIMETHYLHEX-HYDROXYDIPHENYL**, $\text{C}^{12}\text{H}^{14}\text{O}^6 = \text{C}^{12}\text{H}^4(\text{OCH}^3)^3(\text{OH})^3$. This is the brown substance which O. Fischer obtained by the action of sulphuric acid on cœrulignone (p. 549). It differs from hydrocœrulignone, $\text{C}^{12}\text{H}^4(\text{OCH}^3)(\text{OH})^3$, by CH^2 . It yields a triacetyl-derivative having the composition $\text{C}^{12}\text{H}^4(\text{OCH}^3)(\text{O.C}^2\text{H}^3\text{O})^3$ (O. Fischer, *Ber.* viii. 158).

TRIMETHYLACETIC ACID, $(\text{CH}^3)^3\text{C.CO}^2\text{H}$, *Pivalic acid*. See PENTOIC Acids (p. 1501).

TRIMETHYLACETONITRIL, $(\text{CH}^3)^3\text{C.CN}$. Syn. with Tertiary Butyl Cyanide (p. 360).

TRIMETHYLAMINE, $(\text{CH}^3)^3\text{N}$. This base occurs, together with methylamine, in *Mercurialis annua* (E. Schmidt, *Ber.* x. 2228). According to Selmi (*Gazz. chim. ital.* 1876, 468), it is obtained in considerable quantity by the distillation of putrid brain. (On its industrial preparation from the spent wash of the stills in which the molasses of beet-root is distilled for the production of alcohol, and its conversion into methyl chloride, see pp. 1305, 1306).

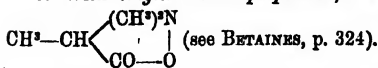
Reactions.—1. By oxidation with *potassium permanganate*, trimethylamine yields carbonic and oxalic acids (Wallach & Claisen, *Ber.* viii. 1237).

2. Trimethylamine heated for twelve hours in a sealed tube on the water-bath with *monochlorhydrin*, is converted into trimethyl-glyceramine (Hauriot, *Compt. rend.* lxxxvi. 1335).

3. Trimethylamine passed in a stream of hydrogen through a red-hot tube yields ammonia, cyanogen, hydrocarbons, hexmethylenamine, $\text{N}[\text{N}(\text{CH}^2)^2]^3$ (iii. 151; vi. 829), which separates from the distillate in crystalline form, and methylenemethylamine, $\text{C}^2\text{H}^3\text{N} = \text{CH}^2.\text{N} = \text{CH}^2$. This last compound is resolved by heating with dilute hydrochloric acid into methyl aldehyde and methylamine, $\text{CH}^3.\text{N} = \text{CH}^2 + \text{H}^2\text{O} = \text{CH}^2\text{O} + \text{CH}^3\text{NH}^2$. It appears, however, from its vapour-density to have the molecular formula $(\text{C}^2\text{H}^3\text{N})^2$ (J. Romeny, *Ber.* xi. 836).

4. When trimethylamine is added to a solution of *aldehyde* in anhydrous ether, water is separated, and condensation-products of aldehyde are formed (N. Lubawin, *Ber.* viii. 1684).

5. With *ethyllic α-chloropropionate*, trimethylamine forms α-propio-betaine,

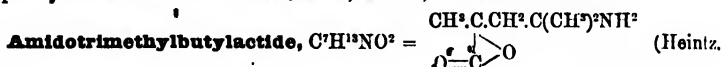


A compound of trimethylamine with *carbon disulphide*, $(\text{CH}^3)^3\text{N}.\text{CS}^2$, is formed by passing trimethylamine-vapour through a mixture of equal parts of carbon disulphide and alcohol. It crystallises in white needles melting at 125° , moderately soluble in chloroform and dilute alcohol, nearly insoluble in absolute alcohol, carbon sulphide, ether, and benzene, and producing a milky turbidity with water. It splits up into its components even at ordinary temperatures, but nevertheless unites with acids (employed in the dilute state) and with salts. With hydrochloric acid it forms the compounds $(\text{CH}^3)^3\text{NCS}^2.\text{HCl}$ and $2(\text{CH}^3)^3\text{NCS}^2.3\text{HCl}$, and analogous compounds with nitric acid and with sulphuric acid. With phosphoric acid it forms the compound $2(\text{CH}^3)^3\text{NCS}^2.\text{H}^3\text{PO}^4$ (A. Bleunard, *Compt. rend.* lxxxvii. 1040).

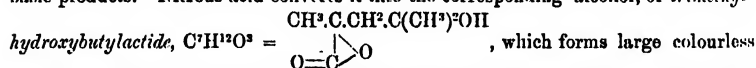
TRIMETHYLANISBETAINÉ, $C^6H^5N(CH^3)^3O^2$, and **TRIMETHYLBENZETAINÉ**, $C^6H^5N(CH^3)^3O^2$; better called *Anisbetaine* and *Benzetaine*. See BETAINES (vii. 187).

TRIMETHYLBENZENE, $C^6H^5(CH^3)^3$. See MESITYLENE and PSEUDOCUMENE (pp. 1282-1285).

TRIMETHYL-BUTYLACTIC (AMIDO-), or **AMIDOTRIMETHYL-HYDROXYBUTYRIC ACID**, $C^7H^{13}NO^3 = CH^3.C(OH)(COOH).CH^2.C(CH^3)^2.NH^2$ (W. Heintz, *Liebig's Annalen*, xcii. 329). This acid is formed by boiling amidotrimethyl-butylactide, $C^7H^{13}NO^2$ (*infra*) with baryta-water, a considerable quantity of the lactide, however, remaining unaltered. On mixing the resulting solution with cupric sulphate, the copper salt of amidotrimethylbutylactic acid is obtained, and this salt decomposed by hydrogen sulphate yields the acid, which is moderately soluble in water, nearly insoluble in alcohol and ether, and when slowly separated from the aqueous solution, crystallises in monoclinic prisms. When heated, it is resolved into water and the lactide. Its silver salt is a stiff gummy mass, the aqueous solution of which is not precipitated by alcohol. The normal sulphate of amidotrimethylbutylactic acid, obtained by dissolving 16 pts. of the amido-acid in water containing 10 pts. of hydrogen sulphate, forms concentric groups of prismatic crystals. The hydrochloride, $C^7H^{13}NO^2.HCl$, obtained by dissolving the amido-acid in hydrochloric acid, forms microscopic needles or square plates. The corresponding nitrate also forms microscopic crystals which are either flat needles, laminae, or six-sided tablets.



Liebig's Annalen, clxxxix. 231; xcii. 339). To prepare this compound, hydrochloride of diacetoneamine (p. 28) is heated with aqueous hydrocyanic acid at 120° for ten hours; the brown product mixed with fuming hydrochloric acid, which throws down, sal-ammoniac; the solution is boiled for six hours in a reflux apparatus and then evaporated; the residue is exhausted with alcohol, the same process being repeated several times upon the extract; and the alcoholic solution is finally dechlorinated with silver sulphate, freed from silver and sulphuric acid by baryta-water, and evaporated down. Amidotrimethylbutylactide thus obtained forms shining prismatic crystals, neutral to litmus, melting above 180° , easily soluble in water and hot alcohol, nearly insoluble in ether, and indifferent to cupric hydroxide and platinic chloride. When heated with hydrochloric acid, it is decomposed with formation of basic products. Nitrous acid converts it into the corresponding alcohol, or trimethyl-



crystals easily soluble in water, alcohol, and ether, and undergoes alteration at 100° , becoming less soluble, and yielding a solution which deposits only small colourless crystalline granules. By boiling with barium hydrate, it is converted into an acid which Heintz regards as trimethyldihydroxybutyric acid.

The action of hydrocyanic acid on diacetoneamine hydrochloride likewise gives rise to three other bodies, viz. *amidobutyric acid*, $C^4H^7NO^2$, *amidotrimethylhydroxybutyronitril*, or *nitrilodiacetonamine*, $C^7H^{14}N^2O$, and the isomeric base, *amidotrimethylhydroxypropylcarbamine* or *carbyldiacetonamine*.

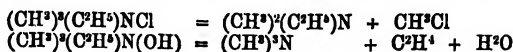
TRIMETHYL-CARBINOL, $(CH^3)^3C.OH$. *Tertiary Butyl Alcohol*.—According to Pawlow (*Liebig's Annalen*, clxxxviii. 118), this compound is best prepared by the action of 1 mol. acetyl chloride on $1\frac{1}{2}$ mol. zinc-methyl, the yield amounting to 79.6 per cent. of the calculated quantity. When heated with dehydrated oxalic acid, it gives up water and yields butylene (Cahours a. Demarcay, *Compt. rend.* lxxxvi. 991).

TRIMETHYL-CARBINYL IODIDE, $(CH^3)^3CI$. On the reaction of this compound with isobutylene in presence of calcium oxide, see TRIBUTYLENE (Iso-) (p. 2044).

TRIMETHYL-CARBINYLAMINE, $(CH^3)^3C.NH^2$, is formed, together with isobutylamine, by heating isobutyl iodide with silver cyanate (R. Brauner, *Liebig's Annalen*, xcii. 65).

TRIMETHYLENE BROMIDE, $CH^2Br.CH^2.CH^2Br$. *Normal Propylene Bromide*.—Julie Lermontoff prepares this compound by saturating allyl bromide at -10° to -15° with dry hydrogen bromide, then heating it for twenty-four hours to 165° – 170° , and repeating the treatment (*Ber.* ix. 1441). (Comp. p. 1672).

TRIMETHYLETHYLAMMONIUM CHLORIDE and **HYDROXIDE** are decomposed by distillation in the manner represented by the following equations:



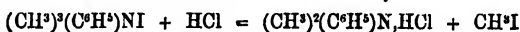
(Lossen, *Liebig's Annalen*, clxxi. 364).

TRIMETHYL-GLYCERAMINE is formed by heating trimethylamino with monochlorhydrin on the water-bath for twelve hours. Its *platinochloride*, $[\text{C}^2\text{H}^5\text{O}(\text{CH}^3)_3\text{N}]_2\text{PtCl}_4$, forms orange-coloured, apparently quadratic tables, which give off hydrogen chloride in a vacuum, and are easily soluble in water, but insoluble in alcohol (Hanriot, *Compt. rend.* lxxxvi. 1335).

TRIMETHYL-MELAMINE, $\text{C}^2\text{H}^3(\text{CH}^3)_3\text{N}^6$, is formed on heating methylcyanamide for a short time in aqueous or alcoholic solution, also when the same compound is exposed to the air, especially to moist air. This reaction explains the production of trimethyl-melamine by disulphuration of methyl-thiocarbamide, as observed by Hoffmann (p. 1271), (E. Baumann, *Ber.* vi. 1371).

TRIMETHYLNAPHTHYLAMMONIUM IODIDE, $\text{C}^{10}\text{H}^7\text{N}(\text{CH}^3)_3\text{I}$. See NAPHTHALENES (AMIDO-), (p. 1370). The corresponding *hydroxide*, obtained by agitating the aqueous solution of the iodide with moist silver oxide, is deliquescent, strongly basic, and forms well-crystallised salts (Landshoff, *J. pr. Chem.* [2], xvii. 286).

TRIMETHYLPHENYLAMMONIUM IODIDE, $(\text{CH}^3)_3(\text{C}^6\text{H}^5)\text{NI}$. This compound, exposed to the action of a stream of dry hydrogen chloride, is converted into dimethylaniline and methyl iodide:



(N. F. Merrill, *J. pr. Chem.* [2], xvii. 286).

TRIMETHYLPHOSPHINE HYDRIODIDE, $\text{P}(\text{CH}^3)_3\text{HI}$. On the formation of this compound from PH^3I and CS^2 , see PHOSPHINES (p. 1579).

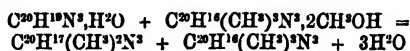
TRIMETHYL- α -PROPIOBETAINE, $\text{C}^6\text{H}^{12}\text{NO}^2$; better called *α -Propiobetaine* (pp. 187, 324).

TRIMETHYL-ROSANILINE, $\text{C}^{23}\text{H}^{23}\text{N}^3 = \text{C}^{20}\text{H}^{16}(\text{CH}^3)_3\text{N}^3$ (A. W. Hofmann, *Ber.* vi. 352). The methochloride of this base is obtained by oxidising dimethylaniline with potassium chlorate and cupric sulphate, or with cupric nitrate and common salt, the ingredients being worked up with sand to a homogeneous mass, and heated, in the first case, in a water-bath for several days, in the second for forty-eight hours at a temperature not exceeding 50° . The free base, the meth-hydroxide of trimethyl-rosaniline, $\text{C}^{20}\text{H}^{16}(\text{CH}^3)_3\text{N}^3.\text{CH}^3.\text{OH}$, separated from the crude product by means of caustic soda-solution, is a blue crystalline precipitate which dries up to a red-brown powder, insoluble in water and in alcohol, but dissolving with fine violet colour in alcohol. It is also readily dissolved by dilute acids, forming salts which are decomposed by ammonia. The *methiodide* obtained from the meth-hydroxide by solution in alcohol and addition of aqueous hydriodic acid, consists of microscopic needles, sparingly soluble in water and in alcohol. The *methylpicrate* forms fine bronze-coloured needles easily soluble in boiling, less easily in cold alcohol. The *leuco-compound*, analogous to the meth-hydroxide of trimethyl-rosaniline, obtained by the action of alcoholic ammonium sulphide on the violet base at 100° under pressure, forms large flattened needles, which acquire a violet tinge in drying, dissolve but sparingly in water, either cold or hot, readily in alcohol and in ether. The results of its analysis agree approximately with either of the formulæ $\text{C}^{20}\text{H}^{16}(\text{CH}^3)_3\text{N}^3.\text{CH}^3.\text{H}$ or $\text{C}^{20}\text{H}^{16}(\text{CH}^3)_3\text{N}^3.\text{H}^2$.

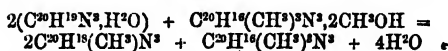
To decide the question whether the violet dye obtained as above from dimethylaniline is identical or isomeric with the methyl-violet prepared on the manufacturing scale from rosaniline, an attempt was made to convert the former into the diiodomethylate. If the two bodies are identical, the diiodomethylate thus produced will be the well-known iodine-green (vi. 162), and convertible by further introduction of methyl iodide into the splendidly crystallised violet tri-iodomethylate. Experiment showed that the bodies in question are identical (Hofmann).

Trimethyl-rosaniline may also be prepared by oxidising a mixture of methylaniline and dimethylaniline with cupric chloride. Rosaniline and trimethylrosaniline

dimethylate act on one another in alcoholic solution at ordinary temperatures, according to the following equations :



and



The colour of the liquid passes from blue through red into violet-red, the last colour changing on addition of hydrochloric acid to leaf-brown (Girard a. Willm, *Bull. Soc. Chim.* [2], xxv. 100).

Triiodomethylrosaniline is prepared by heating a mixture of 10 pts. rosaniline-base, 12 methyl iodide, and 20 methyl alcohol—all as pure as possible—in an enamelled autoclave for three or four hours at a temperature not exceeding 115°. The excess of methyl iodide is then distilled off, and the crystals are purified by recrystallisation (Hofmann, *loc. cit.*)

TRIMETHYLSELENONIUM IODIDE, $(\text{CH}^3)^3\text{SeI}$, is formed when dibenzyl-diselenide (p. 316) is left for two days in a closed vessel with methyl iodide; and on decanting the aqueous solution of the product from a black residue, evaporating slightly, digesting the liquid with silver chloride, and treating the filtrate with platonic chlorides, *trimethylselenonium platinochloride*, $[\text{C}^{12}\text{H}^5]^3\text{SeCl}[\text{PtCl}_4]$, is formed, which crystallises from water in dark red octohedrons (C. L. Jackson, *Ber.* vii. 1277).

TRIMETHYLSULPHINE, $(\text{CH}^3)^3\text{S}$. See SULPHINES (p. 1849).

TRIMETHYL-TOLYLAMMONIUM IODIDE, $(\text{CH}^3)^3(\text{C}^6\text{H}^4.\text{CH}^3)\text{NI}$. See TOLUENES, AMIDO- (p. 2000).

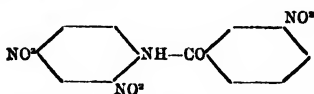
TRINAPHTHALENE-DIAMINE, $(\text{C}^{10}\text{H}^8)^2\text{N}^2$, is formed by heating naphthylamine, naphthylamine hydrochloride, and nitronaphthalene, in molecular proportion, in a sealed tube at 190°–220° for three or four hours. The resulting black mass is pulverised, treating with hot water, and then, after addition of potash-ley, with superheated steam, and the residual base is dissolved in hot alcohol and precipitated by water. It may also be prepared by heating the above mixture in open vessels, the reaction beginning, on addition of a trace of ferric chloride, at 150°. For purification it may be dissolved in chloroform and separated therefrom by evaporation. The base thus obtained contains 1 mol. water, which it gives off slowly at 120°–125°. It is an amorphous blue-black powder, insoluble in water and in ether, dissolving with red colour in warm benzene. Heated at 180° in contact with the air, it begins to decompose. The *hydrochloride*, prepared by passing hydrogen chloride into the chloroform solution, evaporating the chloroform, and washing the residue with hot water, is a violet amorphous powder, dissolving in the same solvents as the base, but more readily and with finer colour. Both the salt and the base produce red-violet colours in dyeing (Salzmann a. Wichelhaus, *Ber.* ix. 1107).

TRI- α -NAPHTHOLPYROMELLITEIC ACID. See NAPHTHOLS (vii. 840).

TRINITRANILINE, $\text{C}^6\text{H}^3(\text{NO}^2)^3\text{NH}^2$ [1 : 2 : 4 : 6, NH^2 in 1]. *Picramide*. See BENZENES, NITRAMIDO- (p. 198).

TRINITROAZOXYBENZENE, $\text{C}^{12}\text{H}^7(\text{NO}^2)^3\text{N}^2\text{O}$. See AZOXYBENZENE (p. 215).

TRINITROBENZANILIDE, $\text{C}^{12}\text{H}^5\text{N}^4\text{O}^7 = \text{C}^6\text{H}^3(\text{NO}^2)^3\text{NH.CO.C}^6\text{H}^4(\text{NO}^2)$, formed by nitration of paranitrobenzanilide, melts at 165°, and is resolvable into metanitrobenzoic acid and [1 : 2 : 4] dinitraniline (p. 198); hence its constitution may be represented by the formula :



The same trinitrobenzanilide is formed from orthonitrobenzanilide (m. p. 94°). Metanitrobenzanilide (m. p. 154°) gives three trinitrobenzanilides melting respectively at 178°, 202°, and 212°. The first of these is resolvable into [1 : 2 : 4] dinitraniline and probably orthonitrobenzoic acid (H. Hubner, *Ber.* x. 1708).

TRINITROBENZENE, $C_6H_3(NO_2)_3$, is obtained by enclosing metadinitrobenzene (p. 176) in proportions of 2 grams each with 20 g. of a mixture of 2 vol. fuming sulphuric acid and 1 vol. highly concentrated nitric acid in strong tubes, and heating the tubes first for a day at 80° , afterwards for two or three days at 130° – 140° . On pouring the contents into water, a precipitate is formed, consisting of trinitrobenzene, which may be purified by crystallisation from alcohol or acetic acid, and then forms white laminae or needles melting at 121° – 122° , slightly soluble in water, more soluble in ether and in hot alcohol (P. Hepp, *Ber.* ix. 402).

Trinitrobenzene forms crystallised compounds with benzene, naphthalene, aniline, and dimethylaniline. By crystallising it from benzene, large prismatic crystals are obtained having the composition $C^6H^3(NO_2)^3 \cdot C^6H^6$. With naphthalene in alcoholic solution it yields the compound $C^6H^3(NO_2)^3 \cdot C^{10}H^8$, which melts at 152° – 153° , and is somewhat unstable, being partly decomposed by recrystallisation from alcohol. The aniline-compound, $C^6H^3(NO_2)^3 \cdot C^6H^5NH_2$, prepared like the last, forms red needles melting at 123° – 124° , nearly insoluble in cold alcohol, and likewise unstable. The homologous dimethylaniline-compound forms long dark violet needles melting at 106° – 108° . By nitrating paradinitrobenzene (m. p. 171°) and treating the product (? an isomeric trinitrobenzene) with aniline and alcohol, a body is obtained melting at 153° , and probably having the composition $C^6H^3(NO_2)^2NHC^6H^5$, together with diazoamidobenzene (Hepp, *Bull. Soc. Chim.* [2], xxx. 4).

TRINITROBENZOIC ACID, $C^6H^2(NO_2)^3 \cdot COOH$, obtained by prolonged digestion of trinitrotoluene with fuming nitric acid at 100° , forms large prismatic crystals melting at 100° , and subliming without decomposition. Its silver salt is sparingly soluble in water (Tiemann & Judson, *Ber.* iii. 223). According to Friedländer (*Zeitschr. f. Kryst.* i. 623), the crystals of trinitrobenzoic acid are orthorhombic. $a : b : c = 0.8870 : 1 : 0.5715$. Combination $\infty P \cdot \infty \bar{P} \infty$ (predominant). $\bar{P} \infty$. Angle $\bar{P} \infty : \bar{P} \infty = 59^\circ 30'$. No distinct cleavage. The plane of the optic axes coincides with OP. The axis b is the first median line. Double refraction positive. Apparent angle of axes in air for Li-red $90^\circ 25'$, for Na-yellow $84^\circ 36'$, for Ti-green $78^\circ 5'$.

TRINITROBENZYLNAPHTHALENE. See NAPHTHALENE (p. 1346).

TRINITROCRESOL, $C^6H(NO_2)^3 \cdot OH \cdot CH_3$. See CRESOLS (p. 583).

TRINITRO- α -DICHLORONAPHTHALENE, $C^{10}H^2Cl^2(NO_2)^3$, obtained by the action of a mixture of strong sulphuric acid and nitric acid (sp. gr. 1.48) on α -dichloronaphthalene, crystallises from glacial acetic acid in brittle yellow prisms, freely soluble in chloroform, sparingly in alcohol, and melting at 178° (O. Widman, *Bull. Soc. Chim.* [2], xxviii. 505).

TRINITRODIETHYLQUINOL, $C^8H(NO_2)^3(OC^2H^5)^2$. See QUINOL (p. 1739).

TRINITRODIMETHYLCATECHOL, $C^6H(NO_2)^3(OH)^2$. See NITROVERATROLS under VERATROL.

TRINITRODIMETHYLETHYLBENZENE, $C^6(NO_2)^3(CH^3)^2(C^2H^5)$. See MESITYLENE, HOMOLOGUES OF (p. 1285).

TRINITRODIMETHYLQUINOL, $C^8H(NO_2)^3(OCH^3)^2$. See QUINOL (p. 1738).

TRINITRODIMETHYLBESORCINOL. See RESORCINOL (p. 1751).

TRINITRODIPHENYL, $C^{12}H^7(NO_2)^3$. This appears to be the composition of a compound formed on dissolving dinitrodiphenyl (p. 661) in a mixture of sulphuric and fuming nitric acids. It separates from solution in benzene in yellowish crystals (Büchner, *Ber.* viii. 22).

TRINITROGLYCERYL is the name given (not very appropriately) by Brackebusch to trinitrin or trinitropropane, $C^3H^5(NO_2)^3$. See GLYCEROL (p. 876).

TRINITROINOSITE, $C^6H^3(NO_2)^3O^4$. See INOSITE (p. 1091).

TRINITROISOXYLENE, $C^8H^7(NO_2)^3$. See XYLENES.

TRINITROMESITYLENE, $C^9H^9(NO_2)^3$. According to Ladenburg (*Liebigs Annalen*, clxxix. 176), this compound, when reduced with tin and hydrochloric acid, yields, not triamidomesitylene, but diamidomesitylene, with separation of ammonia.

TRINITRONAPHTHALENES, $C^{10}H^3(NO_2)^3$. See NAPHTHALENE (p. 352).

TRINITROPARADIPHENYLBENZENE, $C^{18}H^{11}(NO_2)^3$, obtained by the action of fuming nitric acid on paradiphenylbenzene (p. 665), crystallises from glacial acetic acid in long white needles melting at 190° . If the nitration be performed in glacial acetic acid, the chief product is dinitrodiphenylbenzene, which melts at 264° , and is

but sparingly soluble in the ordinary solvents and in glacial acetic acid, even when hot (H. Schmidt a. G. Schultz, *Ber.* xi. 1755).

TRINITROPHENETOIL, $C^6H^2(NO^2)^3.O^2C^2H^3$. See PHENOL-ETHERS (p. 1522).

TRINITROPHENOL, $C^6H^2(NO^2)^3.OH$. See PHENOL (p. 1528).

TRINITROPHENOLSULPHONIC ACID, $C^6H(NO^2)^3(OH)(SO^2H)$. The mother-liquor of barium metabromobenzenesulphonate (p. 236) contains an uncrystallisable barium phenolsulphonate, the acid of which is converted by strong nitric acid into a trinitrophenolsulphonic acid which remains on evaporation as a crystalline mass. Its salts explode violently when heated. The *potassium salt*, $C^6H(NO^2)^3(OH)SO^2K + H^2O$, forms small orange-red rhombic prisms, moderately soluble in water. The *barium salt*, $[C^6H(NO^2)^3(OH)SO^2]^2Ba + 3H^2O$, forms small yellow to reddish-yellow crystals, often grouped in nodules, and moderately soluble in water (Berndsen, *Liebig's Annalen*, clxxvii. 92).

α -TRINITROPHENYLMETANITRANILINE, $NH \begin{cases} C^6H^1(NO^2) \\ C^6H^2(NO^2)^3 \end{cases}$ Syn. with PARAPICRYLMETANITRANILINE. See BENZENES (NITRAMIDO-) (p. 199).

TRINITROPHENYLMETHANE, $CH(C^6H^1.NO^2)^3$. See TRIPHENYLMETHANE (p. 2058).

TRINITRORESORCINOL, $C^6H^2(NO^2)^3(OH)$. See RESORCINOL (p. 1751).

TRINITROSOPHLOOROGLUCOL, $C^6(NO^2)^3(OH)^3$. See PHLOOROGLUCOL (p. 1571).

TRINITROTOLUENE, $C^6H^2(NO^2)^3.CH^3$. See TOLUENE (p. 1994).

TRINITROTOLYPHENYL KETONE, $C^{11}H^4(NO^2)^3O$. See TOLYL KETONES (p. 2038).

TRINITROTRIBROMOBENZENE (symmetric), $C^6.NO^2.Br.NO^2.Br.NO^2.Br$, is formed by the action of a mixture of fuming nitric and sulphuric acids on dinitro-*m*-bromobenzene (p. 181).

TRIPHANE. Pisani (*Compt. rend.* lxxxiv. 1509) has examined a triphane from Brazil, consisting of imperfect crystals which cleave parallel to a prism of $86^\circ 45'$, but do not exhibit the cleavage parallel to $\infty P \infty$, which is so distinct in other triphanes. Hardness = 1; sp. gr. = 3.16. Analysis gave:

SiO ²	Al ² O ³	FeO	MnO	CaO	Li ² O	Na ² O
63.80	27.93	1.05	0.12	0.46	6.75	0.89 = 101.00.

TRIPHENYLACETIC ACID, $(C^6H^5)^3C.COOH$, is formed, together with sal-ammoniac, by the action of fuming hydrochloric and glacial acetic acid on triphenyl-acetonitril (*infra*). It is moderately soluble in alcohol and ligroin, less soluble in glacial acetic acid, and separates from the latter in compact colourless crystals or in thin six-sided laminae or prisms. It softens at 230° , but does not fuse till heated to 260° . It yields a *nitro-derivative* which dissolves with brown colour in alkalis (E. and O. Fischer, *Liebig's Annalen*, xciv. 242).

TRIPHENYLACETONITRIL, TRIPHENYLCARBINYLCYANIDE, or **TRIPHENYLCYANOMETHANE**, $(C^6H^5)^3C.CN$, is formed by the action of dry mercuric cyanide at 150° – 170° on triphenylchloromethane (p. 2057). It crystallises from ligroin or glacial acetic acid in well-defined colourless triangular prisms, which melt at 127.5° , and dissolve readily in hot benzene and glacial acetic acid, less easily in ligroin. Alcoholic potash converts it into a colourless indifferent body, probably a polymeric nitril, which crystallises in colourless needles melting at 210° (F. and O. Fischer).

TRIPHENYLAMINE, $N(C^6H^5)^3$. See pp. 209, 1552.

TRIPHENYLARSINE, $As(C^6H^5)^3$. See PHENYLARSENIC COMPOUNDS (p. 1553).

TRIPHENYL-BENZENE, $C^{24}H^{18} = C^6H^2(C^6H^5)^3$. This hydrocarbon is formed by heating methylphenyl ketone with alcoholic ammonia, and remains undissolved on treating the product with hydrochloric acid. Its formation is a simple process of dehydration, and is analogous to that of mesitylene (trimethylbenzene) from acetone: $3(C^6H^5.CO.CH^3) = 3H^2O + C^{24}H^{18}$. It is also produced by the action of phosphoric anhydride on phenylmethyl ketone (Engler a. Heiner, *Ber.* vi. 638), and by distilling phenyltribenzoic acid over red-hot potassium hydroxide: $C^6H^4(C^6H^4CO^2H)^3 = 3CO^2 + C^{24}H^{18}$ (Gabriel a. Michael, *Ber.* xi. 1007). Engler a. Berthold (*Ber.* vii. 1123) prepare it by saturating phenylmethyl ketone with dry hydrogen chloride and leaving the liquid at rest for several days at a lukewarm temperature, whereupon

triphenylbenzene separates in considerable quantity. A further quantity may be obtained by treating the decanted liquid with hydrogen chloride, and by repeating the operation, a solid product may be obtained amounting in all to about 60 per cent. of the phenylmethyl ketone employed. From the last mother-liquors a further quantity may be precipitated by dilute alkalis.

Triphenylbenzene forms orthorhombic crystals having the axial ratio $a : b : c = 0.56616 : 1 : 0.7663$, exhibiting the combination $\infty \bar{P} \infty . \infty \bar{P} \infty . \infty \bar{P} \infty . \infty \bar{P} \infty$, also (in crystals from another source), $\frac{1}{2} \bar{P}$ and $\frac{1}{2} P$. Fundamental and normal angles, $\infty P : \infty \bar{P} \infty = 60^\circ 29'$; $\bar{P} \infty : \infty P = 72^\circ 33' 30''$. Fracture flat conchoidal, approximating to a cleavage parallel to OP . Plane of optic axes $\infty \bar{P} \infty$. A plate cut parallel to OP showed in air: $2E$ for Li-light = $17^\circ 48'$; for Na-light = $18^\circ 25'$; for Ti-light = $19^\circ 27'$. The double refraction of triphenylbenzene is stronger than that of any other substance yet examined (Arzruni, *Zeitschr. Kryst.* i. 445). On the crystalline form of triphenylbenzene, see also Engler a. Berthold (*loc. cit.*)

Triphenylbenzene melts at 169° – 170° , and boils at a temperature above the boiling point of sulphur. It dissolves sparingly in aqueous alcohol, more readily in absolute alcohol, ether, and carbon sulphide, most readily in benzene (Engler a. Berthold).

Monobromotriphenylbenzene, $C^{12}H^{11}Br$, is formed on leaving a solution of triphenylbenzene and bromine in carbon sulphide at rest for several days, and remains on evaporating the solvent, as a resin which, by crystallisation from alcohol, may be obtained in colourless needles melting at 104° (Engler a. Berthold).

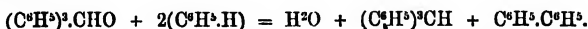
An isomeric of the triphenylbenzene just described is formed, together with resinous products, by the action of strong nitric acid on benzerythrene (vi. 304). Chrysene (vi. 459; vii. 338; viii. 463) has also the same percentage composition (G. Schulz, *Ber.* xi. 95).

TRIPHENYLCARBAMIDE, $NH(C^6H^5).CO.N(C^6H^5)^2$ (see CARBAMIDES, p. 391). It is resolved by heat into phenyl isocyanate and diphenylamine (Michler, *Ber.* ix. 715).

TRIPHENYL-CARBINOL, $C^{19}H^{16}O = (C^6H^5)_3COH$ (Hemilian, *Ber.* vii. 1203). This tertiary alcohol is formed: 1. By boiling trimethylmethane with chromic acid mixture till the oily layer which floats on the surface solidifies to a crystalline crust; it may be purified by washing with boiling water and recrystallisation from benzene. 2. By adding 1 mol. bromine to a solution of 1 mol. triphenylmethane in carbon sulphide. On evaporating the solvent, there remains a brown oil, solidifying when treated with water to a brown mass of the carbinol, which may be freed from brown greasy bodies, and obtained colourless by solution in light petroleum and evaporation of the solvent.

Triphenyl-carbinol melts at 157° , boils at a temperature above 360° , dissolves readily in alcohol, ether, and benzene, and crystallises from these solvents by slow evaporation in shining hard six-sided plates. These crystals, according to measurements by Hintze, belong to the monoclinic system. $a : b : c = 0.75188 : 1 : 0.62971$. Angle $a : c = 119^\circ 41' 50''$. Combination $\infty P . P . OP . -3P \infty . -2P \infty$.

Triphenyl-carbinol is not altered by distillation with soda-lime, or by treatment with alkalis, dilute mineral acids, or sodium-amalgam. It dissolves readily in strong sulphuric acid, even at ordinary temperatures, forming a yellow solution from which it is precipitated by water in its original state. With bromine and nitric acid it forms substitution-products difficult to purify. With acetyl chloride or acetic anhydride, and with benzoyl chloride, it yields ethers which are immediately decomposed by water or by alcohol. The acetic ether when distilled is partially carbonised and yields acetic acid and triphenylmethane. When a solution of the carbinol in anhydrous toluene is boiled with sodium, hydrogen is evolved, and an insoluble, pulverulent, very hygroscopic sodium-derivative is formed, which is immediately resolved by water into sodium hydroxide and triphenyl-carbinol. Triphenyl-carbinol, heated with benzene and phosphoric anhydride, yields triphenylmethane and diphenyl, according to the equation:



Trinitrotriphenyl-carbinol, $C^{19}H^{12}(NO_2)_3.OH$, is formed by oxidising trinitrotriphenylmethane with chromic acid and glacial acetic acid, and separates from hot benzene in nearly colourless crystals melting at 171° – 172° , sparingly soluble in alcohol, ether, and carbon sulphide, more freely in benzene and glacial acetic acid (E. and O. Fischer, *loc. cit.*)

TRIPHENYLCARBINYL CHLORIDE, or **TRIPHENYLCHLOROMETHANE**, $(C^6H^5)_3CCl$, is formed on mixing triphenyl-carbinol with phosphorus pentachloride, the mixture becoming warm and liquefying, giving off hydrogen chloride

and a distillate of POCl_3 , and leaving a residue of triphenylcarbinyl chloride, which solidifies on cooling to a radio-crystalline mass. At 150° this chloride begins to decompose and give off hydrogen chloride. It is slowly decomposed by cold water, instantly by boiling water, yielding hydrochloric acid and triphenyl-carbinol. When heated above 200° , it is resolved into hydrogen chloride and diphenylenephenyl-

methane, $\begin{array}{c} \text{C}^6\text{H}^5 \\ | \\ \text{C}^6\text{H}^5 \end{array} \text{CH} \cdot \text{C}^6\text{H}^5$. By zinc-ethyl, dissolved in benzene, the chloride is converted

into triphenylmethane (E. and O. Fischer). Heated to 150° – 170° with dry mercuric cyanide, it yields triphenylacetoneitril, $(\text{C}^6\text{H}^5)_3\text{C} \cdot \text{O} \cdot \text{CN}$ (p. 2086).

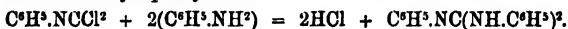
Ethylie Triphenylcarbinylate, or *Triphenyl-ethoxymethane*, $(\text{C}^6\text{H}^5)_3\text{C}(\text{OC}^2\text{H}^5)$, is formed by boiling trimethylcarbinyl chloride with absolute alcohol, and separates, on mixing the cooled product with water, as a colourless oil which solidifies after long standing. It is easily soluble in ether, benzene, and hot alcohol, and separates from the latter in small indistinct crystals which distil without decomposition in a current of air (Hemilian).

TRIPHENYLENE, $\text{C}^{18}\text{H}^{12}$. See CHRYSENE (p. 463).

TRIPHENYLENE-DIAMINE, $(\text{C}^6\text{H}^4)_3\text{N}_2$. This compound is formed, together with sal-ammoniac, by heating 2 mol. aniline with 1 mol. nitrobenzene and dry hydrochloric acid in exhausted tubes for six hours at 230° ; also by heating diphenylamine with nitrobenzene and dry hydrochloric acid at the same temperature for an hour; and by the action of dry hydrochloric acid at 215° on azodiphenyl-blue; it appears to be identical with the colouring matter known as Staedeler's blue (*J. pr. Chem.* xcvi. 63; *Jahresb. f. Chem.* 1865, 410). At the same time an intermediate product, $\text{C}^{18}\text{H}^{13}\text{N}_3$, is formed, which may also be produced by heating aniline hydrochloride with nitrobenzene at 210° (v. Dechen a. Wichelhaus, *Ber.* viii. 1609).

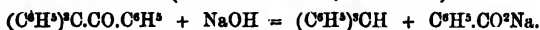
TRIPHENYLETHYLCARBAMIDE, $\text{N}(\text{C}^6\text{H}^5)_3 \cdot \text{CO} \cdot \text{N}(\text{C}^6\text{H}^5)(\text{C}^6\text{H}^5)$. See CARBAMIDES (p. 391).

TRIPHENYL-GUANIDINE, $\text{C}^{19}\text{H}^{17}\text{N}_3 = \text{CH}_2(\text{C}^6\text{H}^5)_3\text{N}_3$. The two known modifications of this compound, α and β , are described under GUANIDINE (p. 906). A body having the same constitution as α -triphenyl-guanidine, but differing from it in physical properties, is described by Sell a. Zierold (*Ber.* vii. 1228) as produced by the action of aniline on isocyanphenyl chloride:



The hydrochloride of this base crystallises from aqueous alcohol in small white laminae melting at 207° , whereas the hydrochloride of α -triphenyl-guanidine obtained by Weith (p. 907) melts at 241° – 242° .

TRIPHENYL-METHANE, $(\text{C}^6\text{H}^5)_3\text{CH}$. This compound, which Kekulé a. Franchimont obtained by heating benzylone dichloride with mercury-diphenyl (vii. 948), is also produced by the following reactions: α . By heating a mixture of benzhydrol, benzene, and phosphoric anhydride at 130° – 140° for four hours. To purify it, the contents of the tube are washed with water and then distilled, whereupon the hydrocarbon passes over at a temperature above 360° as a light yellow oil, solidifying after a while to a mass of crystals, which may be freed from adhering oil by washing with cold, and recrystallisation from boiling alcohol (Hemilian, *Ber.* vii. 1203). β . By heating β -benzpinacolin with soda-lime at about 300° , benzoic acid being formed at the same time (Thörner a. Zincke, *Ber.* xi. 65):



γ . By treating a mixture of benzene and chloroform with aluminium chloride, ferric chloride, or zinc chloride at ordinary temperature, or with ferrous chloride aided by heat (Friedel a. Crafts, *J. pr. Chem.* [2], xvi. 233).

E. and O. Fischer (*Liebigs Annalen*, xciv. 202) prepare triphenyl-methane by mixing 200 g. chloroform and 700 g. dry benzene with aluminium chloride, whereupon a brisk evolution of hydrogen chloride takes place, and afterwards heating the mixture, the reaction being then completed in about thirty hours. On pouring the two resulting layers of liquid into water and applying heat, diphenyl-methane passes over between 200° and 300° , and afterwards triphenyl-methane, which may be purified by crystallisation from alcohol; the pure product amounts to 200 grams.

Triphenyl-methane separates from alcoholic solution in brilliant well-defined crystals, melts at 92.5° , and boils at about 355° .

Trinitrotriphenyl-methane, $(\text{C}^6\text{H}_4 \cdot \text{NO}_2)_3\text{CH}$.—Triphenyl-methane dissolves readily in fuming nitric acid at ordinary temperatures, and on mixing the solution with water, a thick yellow oil is precipitated, which, when treated with chloroform, leaves

the trinitro-compound in the form of a light yellow powder. It is very sparingly soluble in alcohol and ether, easily in boiling acetone and benzene; crystallises therefrom in small yellow scales; melts at 203°, and decomposes without detonation at a higher temperature (Hemilian, *Ber.* vii. 1203). According to E. and O. Fischer (*loc. cit.*) it melts at 206°–207°.

TRIPHENYLMETHANETRISULPHONIC ACID, $\text{CH}(\text{C}^6\text{H}_4\cdot\text{SO}_3\text{H})_3$, formed by the action of sulphuric acid on triphenyl-methane, is very soluble in water, and yields a very soluble barium salt, which is precipitated by alcohol from its aqueous solution, and when air-dried has the composition $[\text{CH}(\text{C}^6\text{H}_4\cdot\text{SO}_3)_2]_2\text{Ba} + 3\text{H}_2\text{O}$. The sulpho-acid, fused with potassium hydroxide, yields a phenolic body easily soluble in ether, and crystallising in colourless needles which, when exposed to the air, quickly turn red and partially resinise (Hemilian).

TRIPHENYL-ROSANILINE, $\text{C}^{20}\text{H}^{16}(\text{C}^6\text{H}_5)_3\text{N}^3$. A body exhibiting the behaviour of this compound is formed, together with HBr and NH_4Br , on gradually adding bromine (6 mol.) to a solution of diphenylamine and toluidine (2 mol. each) in glacial acetic acid, then distilling off the acid, heating the product for some hours at 150°, and afterwards at 180°, till it solidifies and assumes a coppery lustre. The triphenyl-rosaniline may be extracted from the crude product by aniline; purified by dissolving it in 40 pts. alcohol and 2 pts. soda-ley of 20 per cent., and filtering the resulting solution from a brown base formed at the same time; and separated from the filtrate by hydrochloric acid. It dissolves in alcohol with blue colour, and dyes silk like the commercial product 3B. By successive treatment with strong sulphuric acid and caustic soda, it is converted into the form which is soluble in water (A. Weber, *Ber.* x. 760).

On *Triphenylrosaniline-sulphonic acids*, see vii. 77.

TRIPHLORETIDE, $\text{C}^{27}\text{H}^{20}\text{O}^7 = 3\text{C}^9\text{H}^{10}\text{O}^3$ (phloretic acid) $- 2\text{H}_2\text{O}$. Phloretic acid, heated at about 60° with phosphorus oxychloride, dissolves, with evolution of hydrogen chloride, and after about an hour the whole solidifies to a white mass. On washing the product with ether, alcohol, and water, and then dissolving it in glacial acetic acid at the boiling heat, the solution on cooling yields white crystals of triphloretide (H. Schiff, *Ber.* vi. 759).

TRIPHOSPHENYLIC ACID, $(\text{C}^6\text{H}_5)_3(\text{PO})_3\text{O}^3(\text{OH})^2$. See PHOSPHENYLIC ACIDS (p. 1576).

TRIPHOSPHENYL SULPHIDE, $(\text{C}^6\text{H}_5\text{P})_3\text{S}$, is produced, together with phenylphosphine sulphide, $\text{C}^6\text{H}_5\text{P}^2\text{H}^2\text{S}$, by heating phenylphosphine with sulphur at 100° in a stream of hydrogen. It forms crystals which melt at 138°, are insoluble in ether, but dissolve with violent reaction in nitric acid (Köhler a. Michaelis, *Ber.* x. 807).

TRIPHYLIN. This mineral occurs in a granite vein at Grafton, New Hampshire, in masses of various weight up to 20 kilograms and more; frequently decomposed on the outside, but fresh in the interior. The following analyses by S. L. Penfield (*Sill. Am. J.* [3], xii. 425) lead to the formula $10\text{R}^3\text{PO}^4 + 11\text{R}^3\text{P}^2\text{O}^3$, which does not differ much from that given by Rammelsberg (*Mineralchemie*, 2 Aufl. 307), $\text{R}^3\text{PO}^4 + \text{R}^3\text{P}^2\text{O}^3$:

P ² O ⁵	FeO	MnO	CaO	MgO	Li ² O	K ² O	Na ² O	H ² O
44.18	26.09	18.17	0.89	0.56	8.77	0.32	0.16	1.47 = 100.61
43.88	26.38	18.24	0.99	0.61	8.81	0.32	0.09	1.47 = 100.79

TRIPLATOCTONITROSYLIC ACID, $\text{Pt}^2\text{O}(\text{NO}^2)_2\text{H}^4$. See PLATONITHITES (p. 1655).

TRIPLITE. This mineral has been found by Stelzner (*Jahrb. f. Min.* 1874, 304) in the granitic quartz-veins of the Sierra de Cordoba, Argentine Republic, forming masses of the size of the fist without any indication of crystallisation. The analyses, performed by M. Siewert, differ considerably from other analyses of triplite (iv. 571), and are referred by him to the formulæ $(\frac{3}{8}\text{Mn}, \frac{3}{8}\text{Ca})\text{F}^2 + 2[\frac{3}{8}\text{MnO}, \frac{1}{4}\text{FeO}]\text{P}^2\text{O}^3$, for A, and $10[\frac{3}{8}\text{Mn}, \frac{1}{4}\text{Ca})\text{F}^2 + 3(\frac{3}{8}\text{MnO}, \frac{1}{4}\text{FeO})\text{P}^2\text{O}^3] + \text{Fe}^2\text{O}^3$ for B. Sp. gr. of A = 3.24 to 3.86; of B = 3.83 to 3.90.

	X (%)	P ² O ⁵	FeO	Fe ² O ³	MnO	Mn	CaO	Ca	MgO	F
A. 1 (found)	0.13	35.65	18.30	—	37.84	—	4.46	—	trace	4.94 = 101.32
2 (calc.)	—	35.89	18.20	—	35.39	2.55 (*)	—	3.16 (*)	—	4.81 = 100
B. 1 (found)	1.17	31.13	15.88	2.22	37.74	—	5.92	—	trace	7.78 = 101.84
2 (corr.) (*)	—	31.50	16.07	2.25	38.20	—	5.99	—	trace	7.87 = 101.88
3 (calc.)	—	31.21	15.84	3.51	30.77	5.93 (*)	—	4.39 (*)	—	8.35 = 100

(*) Gangue. (**) Equivalent to 3.80 MnO. (*) 4.42 CaO. (°) After deduction of gangue.

(°) 7.69 MnO. (°) 6.14 CaO.

TRIPLOÏDITE (G. J. Brush & E. S. Dana, *Sid. Am. J.* [3], xvi. 33, 114). A ferroso-manganous phosphate, occurring, together with several others, in a granite vein rich in albite, near the village of Branchville, Redding District, Fairfield County, Connecticut. It usually forms crystalline aggregates mostly parallel-fibrous to columnar or divergent, sometimes confusedly fibrous to nearly massive. Occasionally distinct crystals are found imbedded in quartz, from which they cannot be separated without breaking into small pieces; rarely crystals may be found projecting into cavities in the massive mineral. Hardness = 4.5-5. Sp. gr. = 3.697. Lustre vitreous to greasy-adamantine. Colour yellowish to reddish-brown; crystals topaz to wine-yellow, sometimes hyacinth-red. Streak nearly white. Transparent to translucent. Fracture sub-conchoidal.

The crystals are monoclinic and homöomorphous with wagnerite; they are much striated, and occasionally exhibit false planes. Observed faces: $0P$, $\infty P\infty$, $\infty P\infty$, ∞P , $P\infty$, $2P2$. Habit prismatic. Axial ratio $a : b : c = 1.8571 : 1 : 1.4944$. Angle $ac = 71^\circ 46'$. Of the two axes of elasticity which lie in the plane of symmetry, one nearly coincides with the principal crystallographic axis; the other is almost normal to the orthopinacoid.

Analyses by S. J. Penfield: 1. Mean of two analyses of crystals; 2. A darker variety, richer in iron:

	P ₂ O ₅	FeO	MnO	CaO	H ₂ O	Quartz
1.	32.11	14.88	48.45	0.33	4.08	— = 99.85
2.	32.24	18.65	42.96	not det.	4.09	1.09

These analyses lead to the formula $\dot{R}^2P^2O^4 + H^2O = \dot{R}^2(PO)^2 + \dot{R}H^2O^2$, which for Mn : Fe = 3 : 1 requires the values 31.91 P₂O₅, 16.18 FeO, 47.86 MnO, 4.05 H₂O. Triploïdite being isomorphous with wagnerite, and the composition of the latter being analogous to that of triplite, the relations between these three minerals may be represented by the following formulæ:

Wagnerite	Mg ² P ² O ⁸ + MgK ²
Triplite	(Fe,Mn) ² P ² O ⁸ + (Fe,Mn)F ²
Triploïdite	(Mn,Fe) ² P ² O ⁸ + (Mn,Fe)(OH) ²

that is to say, triploïdite is triplite having the fluorine replaced by hydroxyl.

TRIPOLI. This name is given in commerce to a porous, easily friable mineral produced by transformation of hornstone; it occurs in large quantities in South-west Missouri, and is used for making whetstones (A. Schmidt, *Jahrb. f. Min.* 1878, 719).

TRIPROPYLARSINE, (C²H³)³As. See PROPYL-COMPOUNDS (p. 1677).

TRIPROPYLPHOSPHINES, (C²H³)³P. Normal tripropylphosphine is obtained by the action of phosphorus trichloride on zinc-propyl: $3(C^2H^3)^2Zn + 2PCl^3 = 3ZnCl^2 + 2(C^2H^3)^3P$ (Cahours, *Compt. rend.* lxxvi. 1383).

On *Tri-isopropylphosphines*, see PHOSPHINES (vii. 955).

TRIPROPYLSULPHINE IODIDE, (C²H³)³SI. See PROPYL-COMPOUNDS (vii. 1014).

TRIPSEUDOTOLYL-GUANIDINE (see p. 2062).

TRISULPHETHYL-METHANE, or **METHYLTRIMERCAPTIDE**, CH(S.C²H³)³, formed by the action of chloroform on sodium-mercaptide, is an oily liquid, partially decomposing when boiled, and oxidised by nitric acid to ethylsulphonic acid (Niederist, *J. pr. Chem.* [2], xv. 174).

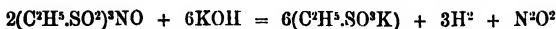
TRISULPHYDROXYBENZOIC ACID, C⁶(OH)H(SO²H)³COOH, syn. with OXY- (or rather HYDROXY-) BENZOTRISULPHONIC ACID (p. 1467).

TRISULPHONETHYL-NITROSYL, C²H³S³O²N = (C²H³.SO²)³NQ. This compound, which Wischin obtained (*Liebig's Annalen*, cxxxix. 364), together with ethylsulphonic acid, by the action of nitric acid on ethylsulphonic acid, C²H³.SO².OH (produced by the action of sulphurous acid on zinc-ethyl), has been further examined by Zuckerschwerdt (*ibid.* clxxiv. 308), who finds that it is more abundantly obtained by treating the product of the action of sulphurous acid on zinc-ethyl directly with nitric acid. The product, which is viscid and ropy, after being freed by a little water from ethyl oxide (formed in its preparation), is gently heated in separate small portions with a large excess of nitric acid of sp. gr. 1.4, whereupon a violent reaction soon sets in, accompanied by evolution of nitrous fumes and separation of an oily liquid, which soon solidifies to a crystalline mass. This mass is separated from the liquid (available for a further operation), pulverised, purified by washing and fusion under water, and

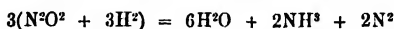
finally twice crystallised from boiling alcohol of 96 per cent. Its formation is represented by the equation:



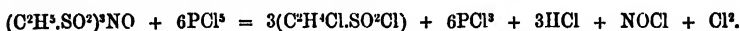
Trisulphonethyl-nitrosyl, when slowly separated from a moderately concentrated alcoholic solution, forms large colourless tabular crystals, easily soluble in boiling alcohol, less soluble in cold alcohol and in ether, very sparingly in cold water, somewhat more freely in hot water. It melts at $81\cdot5^\circ$, volatilises without residue when cautiously heated, and at a higher temperature carbonises and burns, emitting sulphurous vapours. When burnt in a current of air, it gives off large quantities of red vapours. It is not altered by strong sulphuric or hydrochloric acid, even when heated, but by prolonged boiling with nitric acid it yields ethylsulphonic and sulphuric acids. Its alcoholic solution is not precipitated by mercuric chloride, platonic chloride, or silver nitrate. By alcoholic potash at ordinary temperatures, or by aqueous potash at the boiling heat, and more slowly in the cold, or by boiling with baryta-water, it yields ammonia equivalent to one-fourth of the total nitrogen, sulphuric acid, and as chief product (more than 2 mol. to 1 mol. of the substance), ethylsulphonic acid:



and



The oxygen of the NO-group is, however, partly employed in oxidising the ethylsulphonic acid to sulphuric acid. Trisulphonethyl-nitrosyl, heated at 180° with fuming hydrochloric acid, is resolved into ammonia, containing the whole of the nitrogen, and ethylsulphonic acid, while sulphuric acid is formed in relatively small quantity only. The same decomposition takes place, though much more slowly, on heating the compound at 180° with water, the quantity of sulphuric acid thereby produced being relatively greater, and that of ammonia smaller, than in the former case. Heated at 160° with twice its weight of phosphorus pentachloride, the nitrosyl-compound is converted into chlorisethionic chloride:



TRITHIACETALDEHYDE, $\text{C}^6\text{H}^{12}\text{S}^3$. See THIALDEHYDE (p. 1950).

TRITHIACETANILIDE, $\text{C}^8\text{H}^{14}(\text{NH})\text{C}^2\text{H}^5\text{O.S}^3\text{C}^2\text{H}^5(\text{NH})\text{C}^2\text{H}^5\text{O}$, is formed, together with dithiacetanilide, by the action of sulphur chloride on acetanilide at 100° . The two compounds may be separated by means of glacial acetic acid, in which the dithio-compound is easily, the trithio-compound only sparingly soluble. The latter crystallises from solution in glacial acetic acid in nacreous laminae melting at 213° – $214\cdot5^\circ$. It dissolves readily in warm alcohol, and separates therefrom in stellate groups of small crystals (E. B. Schmidt, *Ber.* xi. 1168).

TRITHIOCARBONATE, BUTYLIC, $(\text{C}^4\text{H}^9\text{S})^2\text{CS}$. This thio-ether, formed by heating butyl iodide with a strong aqueous solution of potassium trithiocarbonate at 100° – 130° , is an orange-yellow oily liquid having a faint odour and boiling at 285° – 289° . By alcoholic potassium hydrosulphide at the boiling heat, it is resolved into butyl hydrosulphide, potassium sulphide, and potassium carbonate; by ammonia into butyl hydrosulphide and ammonium thiocyanate (Mylus, *Ber.* vi. 312).

TRITHIONIC ACID, $\text{S}^3\text{O}^6\text{H}^2$. See SULPHUR, OXYGEN-ACIDS OF (p. 1882).

TRITICIN, $\text{C}^{12}\text{H}^{22}\text{O}^{11}$. A gummy substance, isomeric with cane sugar, occurring in the root of couch-grass (*Triticum repens*). See COUCH-GRASS (p. 574).

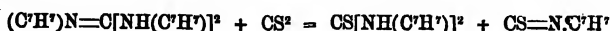
TRITICUM. The pericarp and embryo of common wheat (*Tr. sativum*) have been analysed by A. H. Church (*Arch. Pharm.* [3], x. 60) with the following results:

	Pericarp	Embryo
Water.	15·17	12·53 p. c.
Fat	1·31	4·18
Albuminous matter	10·37	35·70
Cellulose and lignose	70·51	3·12
Starch, dextrin, &c.		38·71
Ash	2·64	5·76

TRITOLYL-ARSIENE, $\text{As}(\text{C}^7\text{H}^7)^3$. See TOLYLARSENIC COMPOUNDS (p. 2031).

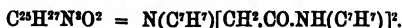
TRITOLYL-GUANIDINE (a), $\text{C}^{22}\text{H}^{23}\text{N}^3 = (\text{C}^7\text{H}^7)\text{N} = \text{C}[\text{NH}(\text{C}^7\text{H}^7)]^2$. Tritolyl-guanidine is formed by heating mono-*p*-tolylcarbamide with *p*-toluidine and PCl^3 (p. 909).

Tri-o-tolyl-guanidine, or *Tripseudotolyl-guanidine*, is obtained by heating diorthotolylcarbamide with PCl_3 and orthotoluidine, or from the corresponding thiocarbamide by heating with *o*-toluidine alone, or in alcoholic solution with *o*-toluidine and lead oxide. It forms cauliflower-like groups of white needles, melts at a little above 100° , is insoluble in water, but soluble in alcohol and ligroin. Heated with carbon bisulphide at 180° , it is resolved into diorthotolylthiocarbamide and orthotolylthiocarbamide:



(E. Girard, *Ber.* vi. 444).

TRITOLYLOXETHYLENE-BIURET,



See GLYCOLLAMIDES (p. 883).

TRIURET, $\text{C}^9\text{H}^4\text{N}^4\text{O}^3$, appears to be formed, together with biuret and phosph-amido-compounds, by the action of phosphorus trichloride on urea (Weith, *Ber.* x. 1743).

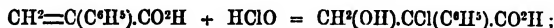
TRIVALERYLENE, $\text{C}^{30}\text{H}^{20}$. See VALERYLENE.

TRÖGERITE, $3\text{UO}^3.\text{As}^2\text{O}^3 + 12\text{H}^2\text{O}$. See URANIC ARSENATES (vii. 1190).

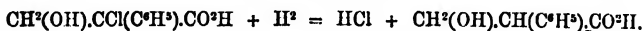
TROPEOLINES. This name is given in commerce to certain yellow and orange colouring matters produced by the action of diazosulphonic acids on phenols. See SULPHONIC ACIDS (p. 1857); further O. N. Witt (*Chem. Soc. J.* xxxv. 179).

W. v. Miller (*Ber.* xi. 460) recommends these dye-stuffs as indicators in alkalimetry. The one best adapted for the purpose is known in commerce as tropeoline 00; its aqueous solution, when treated with acids, acquires a yellow colour changing to crimson, whereas the same coloration is not produced either by acid carbonates or free carbonic acid or solutions of metallic salts.

TROPIC ACID, $\text{C}^9\text{H}^{10}\text{O}^3 = \text{CH}^2(\text{OH}).\text{CH}(\text{C}^6\text{H}^5).\text{CO}^2\text{H}$. This acid, one of the proximate constituents of atropine (vi. 249), has lately been prepared synthetically from atropic acid by Ladenburg a. Rügheimer (*Ber.* xiii. 373). Atropic acid, $\text{C}^9\text{H}^8(\text{O})^2$, treated with hypochlorous acid, is converted into chlorotropic acid, $\text{C}^9\text{H}^8\text{ClO}^2$ (iii. p. 129°):



and this chlorinated acid, which is very soluble in water, is reduced in alkaline solution by zinc-dust and iron-filings to atropic acid:



TROPINE, $\text{C}^9\text{H}^{14}\text{NO}$. This base, which Kraut obtained, together with atropic acid, by the action of baryta-water on atropine, may also be extracted in considerable quantity from the residues of the preparation of atropine. It is likewise produced, together with a brown resinous body called *belladonic acid*, by boiling belladonine with alcoholic potash. Tropine, mixed with benzoyl chloride, yields benzoyl-tropine as an oily mass, which after a while solidifies in the crystalline state, and unites with acids, forming salts very much like those of atropine. The action of tropine on the pupil and on the contractile apparatus of the heart is much weaker than that of benzoyl-tropine or of belladonine (R. Buchheim, *N. Rep. Pharm.* xxv. 344).

TSCHERMAKITE. This triclinic feldspar from Bamle in Norway, analysed with somewhat different results by v. Kobell and by G. W. Hawes (p. 774), has been further examined by Pisani (*Compt. rend.* lxxx. 370), whose analysis agrees nearly with that of Hawes, especially in assigning to the mineral only a small amount of magnesia:

SiO^2	Al^2O^3	CaO	MgO	Na^2O	H^2O	Sp. gr.
66.37	22.70	1.40	0.95	9.70	0.70 = 101.82	2.60

These numbers show that the mineral is an albite, and this result is confirmed by the optical investigations of Des Cloizeaux (*Compt. rend.* lxxx. 364).

TSCHUKING, or **ZERECETITE**, an Abyssinian drug, consisting of the leaves, flowers, and fruit of *Ubyœa Schimperii*, contains, according to Dragendorff (*Aroh. Pharm.* [3], xii. 116):

Moisture	6.11 p. c.
Ash	9.23
Sand	2.81
Ammonia	0.93
Albumin	0.93
Other Proteids	11.74
Cellulose	35.19
Vasculose, Cuticular Substance, &c.	2.57
Pararabin	2.27
Pectin-substance	2.32
Mucus soluble in Water	1.98
Carbohydrate (not Glucose)	11.26
Essential oil	1.72
Fat and a small quantity of Chlorophyll	1.50
Resin and Chlorophyll	2.05
Tannic acid	2.82
Tartaric, Citric, and Oxalic acids	3.61
Oxalic acid combined with lime	0.96
	100.00

TUFA. The tufas of the island of Ischia have been analysed by C. W. C. Fuchs (*Jahrb. f. Min.* 1873, 429): 1. *Green Epomeo tufa*; sp. gr. = 2.17. 2. *Pumice tufa* from Monte di Vico. 3. *Trachytic tufa*: Punta S. Angelo. 4. So-called *Marl*: Epomeo. 5. Mass resembling lithomarge from the so-called *Marl*: Casamicciola di sopra. 6. Clay (so-called): *Creta*; a. Entire mass; b. Soluble in acetic acid; the acetic acid dissolves out 15.44 per cent. CaCO_3 :

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	X (%)
1.	54.69	20.00	3.13	2.26	0.02	2.17	0.70	4.77	0.28	0.021	11.61 = 99.65
2.	54.02	18.18	3.64	2.23	0.11	2.01	0.79	3.86	1.71	0.004	14.30 = 100.85
3.	53.71	16.35	2.82	2.19	0.03	1.38	0.55	6.73	2.53	—	14.43 = 100.72
4.	59.88	17.28	5.06	2.30	trace	1.69	0.80	6.43	2.97	0.043	3.69 = 100.14
5.	58.31	19.79	2.86	2.11	—	0.70	0.81	6.29	2.88	—	7.24 = 100.99
6a.	46.28	12.71	4.46	2.14	—	11.27	2.17	2.58	0.82	—	8.67 = 91.10
6b.	57.20	15.71	5.51	2.64	—	1.16	2.68	3.19	1.01	—	10.71 = 99.81

(¹) Loss by ignition.

Tufa accompanying the diorite of the gold-field of Gympie in Queensland (p. 654) has been analysed by R. Daintree (*Geol. Soc. Qu. J.* xxviii. 271). It contains little or no gold, whereas the diorite is rich in that metal: a. Entire composition; b. Soluble in hydrochloric acid (54.9 p. c.); c. Insoluble (45.1 p. c.):

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	CO_2	H_2O
a.	43.150	21.570	3.610	8.520	12.450	1.785	1.310	1.710	3.560	1.600 = 99.265
b.	28.234	23.442	6.575	11.666	16.074	2.022	—	—	6.484	2.913 = 97.410
c.	60.753	19.395	—	4.800	7.206	1.873	2.904	3.791	—	— = 100.722

The following analyses of tufa-formations in South Tyrol are given by C. Dörlter (*Jahrb. f. Min.* 1873, 569):

1. *Augitic Porphyry* from the Sasso di Mezzodi on the Padoa-peak, designated by v. Richthenhofen as *Eruptive Tufa*; analysed by Epp. 2 and 3. *Pietra verde* from Monte Frisolet near the village of Andraz in the Buchenstein Thal. The name 'Pietra verde' is given to various tufa-formations; in the present case the chemical composition indicates a quartz porphyry tufa: analysed by P. Schridde:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O	P_2O_5	CO_2
1.	53.17	15.57	8.12	2.42	4.83	4.18	3.58	3.22	3.31	1.21	— = 99.66
2.	68.95	10.44	1.30	1.82	5.07	1.47	3.96	2.14	0.60	—	3.74 = 99.49
3.	69.10	10.50	—	3.97	4.62	1.04	7.15	—	—	3.23	—

TUNGSTEN. *Atomic Weight*, 184.—F. Jean (*Compt. rend.* lxxxi. 95) prepares metallic tungsten by mixing finely powdered wolfram with 3 per cent. potassium carbonate and 20–30 per cent. common salt, heating the mixture to redness for half an hour, boiling the cooled and pulverised mass with hydrochloric acid—whereby pure tungsten trioxide is obtained—and reducing this oxide in a stream of hydrogen. F. Filsinger (*Chem. Ind.* 1878, 229) prepares the metal from commercial sodium tungstate by adding 1 pt. of the salt to 2 pts. by weight of common hydrochloric acid of sp. gr. 1.18 to 1.19, passing steam into the liquid till it boils; then adds nitric acid

of sp. gr. 1.35 in quantity equal to 4 or 5 per cent. of the sodium salt; and continues the boiling till the separated tungstic oxide assumes a dark yellow colour. This oxide, after being thoroughly washed and dried, is ultimately mixed with 10 per cent. finely powdered charcoal, and 2 or 3 per cent. powdered rosin, and heated to whiteness for several hours in a well-closed crucible. The product, when pulverised and freed from charcoal by levigation, yields 80–90 per cent. metallic tungsten.

On the Estimation of Tungsten in Iron and Steel, see S. Kern (*Chem. News*, xxxv. 67, 247, 270).

On the Technical Applications of Tungsten and its Compounds, see J. Philipp (*Hofmann's Entwicklung der Chemischen Industrie*, 745).

Chlorides and Oxychlorides. Persoz n. Bloch (*Compt. rend.* xxviii. 86, 289), by heating tungsten trioxide with phosphorus pentachloride at 200°, obtained a product to which they assigned the formula $WO_2 \cdot 2PCl_5$, and H. Schiff (*Liebig's Annalen*, cii. 211) obtained by the same reaction a product which he regarded as a compound of $POCl_3$ with WO_2Cl_2 . According to N. Teclu, on the other hand (*ibid.* clxxxvii. 255), the sole products of this reaction are phosphorus oxychloride and tungsten hexachloride, WCl_6 , which is thus obtained in metallicallly lustrous steel-blue crystals, melting at 189°, easily soluble in phosphorus oxychloride, retaining their metallic lustre undiminished when immersed in water of ordinary temperature even for thirty-six hours, and exhibiting in other respects the properties assigned to the compound by Roscoe (vii. 1184).

Further experiments on the action of PCl_5 on WO_3 have been made by Schiff a. Piutti (*Gazz. chim. ital.* ix. 277), who find that, under the conditions described by Teclu, the hexachloride is the only product obtained, but that under other conditions oxychlorides are likewise produced. When the trioxide (prepared from ammonium tungstate) is heated in a retort with 1 or 2 mol. PCl_5 , phosphorus oxychloride distils over, together with a small quantity of the higher chlorides of tungsten, chiefly the hexachloride. The red-brown residue is washed with cold carbon sulphide to remove small quantities of hexachloride, and then treated with a larger quantity of warm carbon sulphide, which dissolves up the tungsten oxychlorides, leaving a residue of unattacked tungsten trioxide and lower chlorides of tungsten. A portion of the oxychlorides separates in red crystals on cooling, but the greater part remains dissolved, and is obtained as a crystalline cake on evaporating the carbon sulphide. By careful sublimation in a stream of carbon dioxide, the more volatile oxytetrachloride, $WOCl_4$, may be separated from the less volatile yellow dioxydichloride, WO_2Cl_2 . When 1–2 mol. PCl_5 is employed to 1 mol. WO_3 , the chief product of the reaction is the oxytetrachloride, which, when purified by sublimation, is sometimes obtained in splendid red needles melting at 208°–210°. By heating with PCl_5 to about 170°, it is converted into the hexachloride, a small portion of which is resolved into chlorine and the pentachloride.

A mixture of tungsten oxychlorides is obtained by heating the trioxide to redness in a stream of the vapour of carbon tetrachloride, or in a stream of chloride and carbon dioxide previously passed over red-hot charcoal (C. W. Watts a. C. A. Bell, (*Chem. Soc. J.* xxxiii. 360).

Trioxide or Tungstic Oxide, WO_3 , and Tungstates. On the preparation of the pure trioxide from commercial sodium tungstate, see p. 2063.

The following reactions of soluble tungstates are described by J. W. Mallet (*Chem. Soc. J.* xxviii. 1228): 1. Contrary to the statements in many manuals, the precipitate formed by hydrochloric acid in an alkaline tungstate is redissolved by an excess of strong hydrochloric acid. 2. Such a solution gradually brought in contact with small pieces of zinc exhibits various colours, the most striking of which is a brilliant magenta-red. 3. On treating the hydrochloric acid solution with potassium thiocyanate, and then introducing a piece of zinc, a deep green colour is produced. 4. When, on the other hand, the solution of an alkaline tungstate is treated first with potassium thiocyanate, then with hydrochloric acid and zinc, a fine amethyst colour is produced. 5. The blue colour characteristic of the lower oxides of tungsten is best obtained by reduction with hypsulphurous acid, SO_2H_2 .

According to O. Maschko (*Zeitschr. anal. Chem.* 1877, 427), a strongly alkaline solution of sodium tungstate is reduced and turned blue by organic bodies.

On the reaction of sodium tungstate with sal-ammoniac, see F. Jean (*Compt. rend.* lxxviii. 1436; *Jahresh. f. Chem.* 1874, 283).

Tungsto-sodic Tungstate (gold-bronze) is best prepared by adding tungstic oxide to a mixture of tin and acid sodium tungstate, in such quantity that the mixture when fused in a crucible at a rather strong heat, then pulverised and introduced into a porcelain tube, merely sinters together over a weak charcoal fire. Reduction by means of coal-gas then takes place in a few hours. After repeated purification with

hot nitric acid to oxidise the excess of tungsten dioxide, and with soda-ley, the preparation forms a powder having in sunlight a splendid gold-yellow colour. The corresponding potassium-salt (violet-bronze) requires a higher temperature (H. Schnitzler, *Dingl. pol. J.* cexi. 484).

Acid Tungstates (J. Lefort, *Compt. rend.* lxxxvii. 748; lxxxviii. 798; *Ann. Chim. Phys.* [5]. xvii. 470).—The following acid tungstates of potassium and sodium are obtained by the action of organic acids on the corresponding normal tungstates. *Sodium ditungstate*, $\text{Na}^2\text{W}^2\text{O}_7 \cdot 6\text{H}^2\text{O}$, is obtained in fine long prismatic crystals on adding acetic acid to a solution of the normal tungstate till the liquid exhibits an acid reaction. The *tritungstate*, $\text{Na}^2\text{W}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is easily prepared by pouring a boiling-hot solution of the ditungstate into boiling acetic acid. The liquid, if left in a cold place, separates into two layers, the lower of which—heavy, semi-transparent, syrupy, and difficult to crystallise—contains the tritungstate, while the upper consists chiefly of sodium acetate and excess of acetic acid. The *tritungstate* crystallises in elongated prisms. A salt, $\text{Na}^4\text{W}^3\text{O}_{17} \cdot 11\text{H}^2\text{O}$, intermediate between the two preceding, is obtained in oblique prisms on adding a solution of the normal tungstate to acetic acid. Corresponding *potassium salts* are obtained in like manner: $\text{K}^2\text{W}^2\text{O}_7 \cdot 3\text{H}^2\text{O}$ crystallises in nacreous laminæ; $\text{K}^2\text{W}^3\text{O}_{10} \cdot 2\text{H}^2\text{O}$, in small very slender needles; $\text{K}^4\text{W}^3\text{O}_{17} \cdot 2\text{H}^2\text{O}$ in prismatic tablets, easily resolved by boiling water into the di- and tri-tungstate. The tritungstate of potassium is especially distinguished by its property of being transformed into the metatungstate by prolonged boiling with acetic acid, a character not exhibited by the corresponding sodium salt.

Oxalic acid converts the normal tungstates of potassium and sodium into ditungstate and oxalate, which, in the case of the sodium salts, crystallise together and cannot be separated, whereas the potassium salts are easily separated in consequence of the relatively sparing solubility of the ditungstate. The action of *tartaric acid* on normal alkali-tungstates appears to give rise to uncrystallisable double salts; *citric acid* also produces double salts, one of which crystallises in tufts of oblique prisms.

The following tritungstates are obtained by mixing the solution of sodium tritungstate with an equivalent quantity of a metallic acetate, and leaving the mixture at rest for some time. Excepting in the case of the barium, strontium, and lead salts, which are but slightly soluble in water, no precipitation takes place at first, but on addition of alcohol the salts separate in the form of bulky precipitates which aggregate into semi-transparent and semi-solid viscid masses. The tritungstates are for the most part unstable, and easily decompose, especially in aqueous solution, into insoluble ditungstates and soluble tetratungstates. They are also decomposed by mineral acids, and in the first instance without separation of tungstic acid, the formation of the hydrate of that acid taking place only after some hours.

Barium Tritungstate, $\text{BaW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, or $\text{BaO} \cdot 3\text{W}^3\text{O}_3 \cdot 4\text{H}^2\text{O}$, is a white bulky amorphous precipitate, soluble in about 300 pts. water at 15° ; it is not decomposed by cold water, but is resolved on boiling into insoluble di- and soluble tetratungstate. The *strontium salt*, $\text{SrW}^3\text{O}_{10} \cdot 5\text{H}^2\text{O}$, separates as a white bulky precipitate, which coagulates to a colourless viscid mass. The *calcium salt*, $\text{CaW}^3\text{O}_{10} \cdot 6\text{H}^2\text{O}$, is a white semi-solid glutinous precipitate, soluble in cold water. The *magnesium salt*, $\text{MgW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is a white glutinous mass very soluble in water. The *manganous salt*, $\text{MnW}^3\text{O}_{10}$, is a wax-yellow translucent pasty mass. The *ferrous salt*, $\text{FeW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is a reddish precipitate which coagulates to a brown pasty mass, and quickly oxidises in moist air. The *nickel salt*, $\text{NiW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is a greenish-white mass of the consistence of honey. The *cobalt salt*, $\text{CoW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is a reddish viscid mass. The *cadmium salt*, $\text{CdW}^3\text{O}_{10} \cdot 4\text{H}^2\text{O}$, is a white semi-transparent gummy mass. The *lead salt*, $\text{PbW}^3\text{O}_{10} \cdot 2\text{H}^2\text{O}$, is a white pulverulent precipitate which does not become viscid. Neither a cupric nor a mercurous tritungstate appears to exist.

The following tungstates have also been prepared by Lefort (*loc. cit.* 748; lxxxviii. 798). *Aluminium Salts*.—The *normal salt*, $\text{Al}^2\text{O}_3 \cdot 3\text{W}^3\text{O}_3 \cdot 8\text{H}^2\text{O}$, is obtained by precipitating alum-solution with normal sodium tungstate, as a white bulky precipitate soluble in 1500 pts. water at 15° . An *acid salt*, $\text{Al}^2\text{O}_3 \cdot 4\text{W}^3\text{O}_3 \cdot 9\text{H}^2\text{O}$, formed on mixing the concentrated aqueous solutions of alum and acid sodium tungstate, is a white, much denser precipitate, soluble in 400 pts. water at 15° . Another acid salt, $\text{Al}^2\text{O}_3 \cdot 5\text{W}^3\text{O}_3 \cdot 6\text{H}^2\text{O}$, is obtained on mixing aluminium acetate and sodium tritungstate in equivalent proportions, as a white precipitate which thickens to the consistence of honey. *Ferric salts*.— $2\text{Fe}^2\text{O}_3 \cdot 3\text{W}^3\text{O}_3 \cdot 6\text{H}^2\text{O}$ is obtained by precipitating ferric acetate with normal sodium tungstate, as a yellow precipitate, soluble in about 300 pts. water at 15° . $\text{Fe}^2\text{O}_3 \cdot 2\text{W}^3\text{O}_3 \cdot 4\text{H}^2\text{O}$, obtained in like manner with sodium ditungstate, is a brown-yellow precipitate soluble in about 50 pts. of water. $\text{Fe}^2\text{O}_3 \cdot 4\text{W}^3\text{O}_3 \cdot 4\text{H}^2\text{O}$ is obtained by precipitation with sodium tritungstate as a deep-red pasty mass. *Chromic salts*.—The *basic salt*, $\text{Cr}^2\text{O}_3 \cdot 2\text{W}^3\text{O}_3 \cdot 5\text{H}^2\text{O}$, is obtained with chromic acetate and normal

sodium tungstate, as a blue-green powder soluble in 400 pts. water at 15° the *normal salt*, $\text{Cr}^2\text{O}^3 \cdot 3\text{WO}^3 \cdot 3\text{H}^2\text{O}$, by precipitating chrome-alum with sodium ditungstate, as a dingy green powder; an *acid salt*, $\text{Cr}^2\text{O}^3 \cdot 4\text{WO}^3 \cdot 6\text{H}^2\text{O}$, by mixing the solutions of chromic acetate and sodium ditungstate, and pouring the mixture into strong alcohol; and another acid salt, $\text{Cr}^2\text{O}^3 \cdot 5\text{WO}^3 \cdot 5\text{H}^2\text{O}$, with chromic acetate and sodium tritungstate, as a bluish translucent viscid mass. *Antimony salts*.—The *normal salt* appears to be formed on mixing a solution of tartar-emetic with normal sodium tungstate, as a white precipitate slowly decomposed by washing with water. An *acid salt*, $\text{Sb}^2\text{O}^3 \cdot 5\text{WO}^3 \cdot 4\text{H}^2\text{O}$, is formed on mixing the solutions of tartar-emetic and sodium ditungstate, as a heavy yellowish precipitate which dissolves in water with moderate facility and without decomposition. Another acid salt, $\text{Sb}^2\text{O}^3 \cdot 6\text{WO}^3 \cdot 8\text{H}^2\text{O}$, is obtained as a white precipitate on mixing the solutions of tartar-emetic and sodium tritungstate. The *bismuth salt*, $\text{Bi}^2\text{O}^3 \cdot 6\text{WO}^3 \cdot 8\text{H}^2\text{O}$, obtained in like manner with bismuth acetate, is also a white precipitate. *Uranic salts*.—The *basic salt*, $\text{UO}^3 \cdot \text{WO}^3 \cdot 2\text{H}^2\text{O}$, is a yellow amorphous sparingly soluble precipitate; the *normal salt*, $\text{UO}^3 \cdot 3\text{WO}^3 \cdot 5\text{H}^2\text{O}$, is a yellow amorphous precipitate (Lefort).

Lanthanum Tungstate, $\text{La}^2\text{O}^3 \cdot 3\text{WO}^3$, obtained on mixing sodium tungstate with a lanthanum salt, is a colourless gelatinous precipitate which dries up at the heat of a water-bath to a thick white crust, soluble in acids. The *didymium salt*, $\text{Di}^2\text{O}^3 \cdot 3\text{WO}^3$, is obtained in like manner as a gelatinous precipitate, which dries up to a transparent rose-coloured mass (Frerichs a. Smith, *Liebig's Annalen*, xcxi. 331).

Native Tungstates.—Wolfram and Scheelite, occurring at Meymac, Département Corrèze, France, have been analysed by A. Carnot (*Compt. rend.* lxxix. 637). 1–3. *Wolfram*. Sp. gr. = 6·54. 1 and 2. Black shining fragments with brown streak. 3. Laminar black, with greyish veins; streak grey. 4 and 5. *Scheelite*:

	WO ³	FeO	MnO	CaO	MgO	Ta ² O ⁵	Gangue	H ² O	
1.	74·75	16·17	6·40	0·40	0·17	0·95(1)	1·12	—	= 99·96
2.	74·25	16·85	6·51	0·80	0·04	1·10(1)	—	0·70	= 99·25
3.	72·67	14·70	3·38	0·70	traco	0·90(1)	4·00	1·55	= 97·90
4.	74·50	1·05	0·30	18·70	—	—	5·20	—	= 99·75
5.	74·20	1·51	0·35	18·84	—	0·40	4·24	—	= 99·54

(1) In other specimens the proportion of Ta²O⁵ rose to 5 per cent. (2) Fe²O³. (3) Mg²O³.

On the Crystalline Form of Wolfram, see Jeremjew (*Jahrb. f. Min.* 1873, 421); Groth a. Arzruni (*Pogg. Ann.* cxlix. 235); Krenner (*Jahrb. f. Min.* 1875, 648); also *Jahresh. f. Chem.* 1873, 1184; 1875, 1232.

On *Platinotungstates*, see PLATINUM (p. 1656).

TURMERIC. This substance may be detected in rhubarb and mustard by exhausting these latter with absolute alcohol and mixing the yellow filtrate with borax. If turmeric is present, the solution acquires a deep red-brown colour, the intensity of which is scarcely diminished by addition of hydrochloric acid (Mensch, *Dingl. pol. J.* cccviii. 80). L. Howie (*Arch. Pharm.* [3], v. 251) places the pulverised mustard or rhubarb on white paper, and moistens it with a few drops of chloroform. This liquid on evaporating leaves the powder surrounded with a yellow ring of various depths of colour; and on placing thereon a drop of concentrated borax solution and a drop of hydrochloric acid, the presence of turmeric will be detected by the production in a few seconds of a decided red colour, changing on addition of potash-ley to a black or greenish-black.

TURNERITE. The native cerous phosphate called by this name has been shown to be identical with monazite. See PHOSPHATES (p. 1599).

TURNBULL'S BLUE, $\text{Fe}(\text{CN})^{12}$. On the occurrence of this pigment in commercial Prussian blues, see FERROCYANIDES (p. 614).

TURPENTINE. See TERPENES (p. 1901).

TURQUOISE. H. Bucking (*Jahrb. f. Min.* 1878, 655) has examined turquoises from the Megara Valley, Sinai, Nicabar in Persia, Moses Well in Arabia, Steine in Silesia, Oelsnitz in Saxony, and Silver Peak, Columbus District, Nevada. The nature of the colouring matter in these turquoises has not been determined with certainty. The mass is for the most part homogeneous, made up of very small double-refracting particles, and when examined by ordinary light, exhibits darker-coloured annular portions in some specimens only (especially those from the Megara Valley); in polarised light, on the other hand, especially in specimens exhibiting incipient decomposition, chalcedony-like particles having a concentrically scaly structure may be detected most abundantly in the German specimens. The so-called 'Persian turquoise' lately introduced into commerce, and often regarded as an artificial product,

approaches most nearly to the American, and may be recognised as genuine by the brown hæmatite which adheres to it and penetrates the mass; it is perhaps a particularly fresh variety from Nicabur. Sections of turquoise when heated turn first green, then black, and finally brown, a reaction which indicates copper phosphate as the admixed pigment. According to J. J. Pohl (*Jahrb. f. Min.* 1878, 364; *Chem. Soc. J.* xxxvi. 209), genuine turquoises may be distinguished with certainty from imitations by the decrepitation which they exhibit when heated.

TYROLEUCINE. See PROTEINS (p. 1682).

TYROSINE, $C^6H^9NO^3$, probably $C^6H^4(OH).C^2H^3(NH^2).COOH$. This compound occurs, together with aspartic acid, glutanic acid, and leucine, in pumpkin-sprouts (Schulze a. Barbieri, *Ber.* xi. 710); also in yeast (Schützenberger, *Compt. rend.* lxxviii. 943). It is formed, together with leucine and volatile fatty acids, by the action of melting potash on albumin, but is decomposed if the action be prolonged, with formation of phenol (Nencki, *J. pr. Chem.* [2], xvii. 97). It is also produced in the decomposition of albumin and gelatinous substances by pancreatic ferments in closed vessels (Jeanneret, *ibid.* xv. 353). On its formation from proteids by heating with baryta-water, see p. 1682. By fusion with sodium hydroxide it is converted into para-hydroxybenzoic acid (Ost, *J. pr. Chem.* [2], xii. 159). By oxidation with potassium permanganate in ammoniacal solution, it is converted into ammonium carbamate (Drechsel, *ibid.* xii. 417).

Copper-tyrosine, $(C^6H^9NO^3)^2Ca$, obtained by adding cupric hydrate to a saturated solution of tyrosine, crystallises in shining needles soluble in 1230 pts. cold and 240 pts. boiling water (F. Hofmeister, *Liebig's Annalen*, clxxxix. 6).

U.

ULMIC SUBSTANCES. On the relation of these bodies to the Azo-compounds, see DIAZOXYBENZOIC ACID (p. 278).

On the formation of Ulmic substances from Sugar by the action of Acids, see Sestini (*Gazz. chim. ital.* 1880, 121; *Chem. Soc. J.* xxxviii. 538).

On the formation of a black liquid resembling the ulmic compounds by the electrolysis of a 5 per cent. solution of ammonia with a cathode of platinum and an anode of gas-carbon, see Millot (*Compt. rend.* xc. 611; *Chem. Soc. J.* xxxviii. 482).

ULMUS. The flowers of the common elm (*U. campestris*) have been analysed by A. H. Church (*Journal of Botany*, March 1876; *Arch. Pharm.* [3], x. 60). The female flowers gathered in May gave, after drying, 8.15 per cent. ash and 3.31 nitrogen. 100 pts. of the ash contained:

CaO	K ² O	P ² O ⁵	SO ²	SiO ²
13.95	29.27	11.95	16.39	5.57

100 pts. of the dry flowers yielded:

C, H, O	N	K ² O	P ² O ⁵	SO ²	SiO ²	CaO, &c.
88.54	3.31	2.39	0.97	1.34	0.40	3.05

ULTRAMARINE. *Manufacture and Constitution.*—From an examination of the influence of the relative proportions of silica and alumina on the formation of ultramarine, C. Böttger (*Liebig's Annalen*, clxxii. 305) infers that these proportions may vary within somewhat wide limits without making any essential difference in the quality of the product, provided that a certain proportion between the silica and sulphur be not exceeded.

A series of experiments on the influence of varying proportions of soda to sulphur led to the conclusion that ultramarine may be regarded as the last term of a series of molecular compounds of an aluminium silicate with a sodium silicate in which the oxygen is more or less replaced by sulphur. The same view is taken by Fürstonauf (*Dingl. pol. J.* cccix. 269), who also finds that only two aluminium silicates are adapted for the preparation of ultramarine, viz. $4Al^2O^3.9SiO^2$ and $Al^2O^3.3SiO^2$. These, when treated with di- or pentasulphide of sodium, give pigments having the following properties: (a) $4Al^2O^3.9SiO^2$ with Na^2S^2 : pure clear blue, but with little colouring power; (b) $4Al^2O^3.9SiO^2$ with Na^2S^3 : pure dark blue, with great colouring power; both these products are free from alum. (c) $Al^2O^3.3SiO^2$ with Na^2S^2 forms a light reddish somewhat dingy-coloured product; and (d) with Na^2S^3 , a product having a dark violet-blue colour and great tinctorial power; both these ultramarines contain alum.

In selecting a kaolin for the preparation of ultramarine, care must be taken that it does not contain any untempered clay or finely divided stony matter, as such clays always yield muddy colours. The proportion of silica may be adjusted by addition of very finely ground and levigated quartz and ignited siliceous earth (*Kieselguhr*). The following proportions have been found to give good results: (1) for blue wares: $4\text{Al}^2\text{O}^3, 9\text{SiO}^2 + 8\text{Na}^2\text{CO}^3 + 8\text{C} + 14\text{S}$, and (2) for reddish aluminiferous strongly colouring sorts: $\text{Al}^2\text{O}^3, 3\text{SiO}^2 + 4\text{Na}^2\text{CO}^3 + 8\text{C} + 16\text{S}$. If in the first of these mixtures the sodium carbonate be replaced by sulphate and charcoal (so that the oxygen is given off as carbon oxide), light colours with little tinctorial power will be produced.

Whether the calcination is performed in reverberatory furnaces or in pots, a single burning is not sufficient to produce a perfectly blue ultramarine. For this reason, three-staged furnaces have come into use, the lowest stage being used for the ignition, the other two for the blue-burning and drying. A charge of 30 to 35 cwt. requires eighty-six hours' heating before raking out, and ten days for cooling. A reverberatory furnace yields about 15 cwt. of blue ultramarine in fourteen days. To obtain a purer product in shorter time, Fürstenau proposes to conduct the process in a pot-furnace capable of holding from 64 to 80 kg. of the mixture. This furnace may be raked out after eight hours at the latest, requires two days for cooling, and yields 25 cwt. green ultramarine convertible into 18.57 cwt. blue, the rate of production being 47 cwt. blue in fourteen days. The green product is converted into the blue by roasting with sulphur in the usual way.

The relation between blue and green ultramarine has been investigated by J. Philipp (*Ber.* ix. 1109). When green ultramarine is heated with water at 100° in sealed tubes, it assumes a fine bright blue colour; its weight, however, remains nearly the same—the water taking up only a small quantity of sodium compounds—and its composition is unaltered. Moreover, the sulphur exists in the same state in blue ultramarine prepared in the wet way as in the green ultramarine from which it has been produced. The formation of blue ultramarine is therefore in no way dependent upon the oxidation of sulphur, but the difference between the two ultramarines is due to the presence in the green substance of a small quantity of sodium sulphide, either mechanically mixed or chemically combined, on the removal of which the blue colour appears. Green ultramarine may indeed be actually formed by fusing blue ultramarine with sodium sulphate and charcoal.

Comparative analyses of Blue, Green, and Violet Ultramarine have been published by E. Dollfus and F. Goppelsröder (*Bull. de Mulhouse*, 1875, Mai; *Dingl. pol. J.* cxxx. 337, 431).

	Green	Blue	Violet
Silicon	17.063 p. c.	19.160 p. c.	20.440 p. c.
Aluminium	17.702	13.925	12.735
Sodium as Na^2O	10.487	10.088	11.110
Potassium	0.420	—	—
Sulphur as SO^3	0.292	0.500	0.877
Sulphur as SO^2	0.213	0.441	0.834
Sulphur as S^2O^2	—	0.469	2.536
Sulphur as Na^2S	3.718	3.057	1.165
Free sulphur	3.491	8.977	6.964
Sodium as Na^2	5.345	4.395	1.676
Oxygen	40.363	38.984	41.748
	99.994	99.996	100.086

The behaviour of these three ultramarines to various reagents is given in the following table (p. 2070) in which the numbers placed after each colour denote the more or less rapid progress of the action. 0 denotes no reaction; 1, slow; 2, moderately quick; 3, quick; 4, very quick.

A violet ultramarine from the Vienna exhibition has been examined by Lussy (*Ber.* viii. 979). It appeared homogeneous under the microscope, was acted upon by acids and by alum solution, but resisted the action of ammonia and sodium carbonate. Caustic soda extracted sulphur and silica from it, and changed its colour to blue. Previous to quantitative analysis it was exhausted with water, which dissolved out 12.85 per cent. sodium sulphate without altering the colour. Thus purified, it gave:

SiO^2	SO^2	Al^2O^3	Na^2O	CaO	$\text{S} (^)$	$\text{S} (^)$
47.23	1.88	20.93	19.28	1.97	0.82	9.25 = 100.36

(¹) Expelled as H^2S . (²) Determined as BaSO^4 in the residue.

100 pts. of this violet ultramarine lost by boiling with soda-ley 12·44 per cent. silica and 0·62 sulphur, and the residual mass exhibited exactly the composition and reactions of blue ultramarine.

According to R. Hoffmann (*Chem. Industrie*, 1878, 304), blue and green (so-called white) ultramarine are converted, by the action of acids at high temperatures, or of salts which give up their acid at high temperatures, into purple-red or violet colouring matters, which when further heated with acids, with or without access of air, are converted into a red.

G. Scheffer (*Ber.* vi. 1450) observes that in the preparation of ultramarine a yellow body is sometimes produced, which, as the operation proceeds, is converted into red, violet, and then suddenly into blue ultramarine. The final product having been freed by water from sodium sulphate was found to contain 28·83 pts. yellow to 24·50 red, and 17·95–19·32 ultramarine. The undissolved masses contained:

	Yellow	Red	Blue
SiO ²	49·55	46·35	49·38–50·64
Na	8·97	9·33	11·90–12·00
Al ² O ³	22·13	23·20	20·95–26·95
Sa	13·22	13·96	14·42–13·46
Sb	12·27	12·15	12·00–11

Sa is the total quantity of sulphur; Sb the amount remaining after decomposition of the substance by hydrochloric acid. Free sulphur, removable by extraction with carbon sulphide or by roasting, is found only in the blue. E. Büchner (*Ber.* vii. 989) regards these yellow and red bodies as products of the decomposition of blue ultramarine at high temperatures.

According to Unger (*Ber.* v. 989), ultramarine contains nitrogen, and has the composition Al²Si²O³N², the sodium used in its manufacture being eliminated in the course of the reaction as sulphide and sulphate. The nitrogen is supposed to be derived partly from the air, partly from the sal-ammoniac with which the green ultramarine is sometimes heated to convert it into the blue. On the other hand, W. Morgan (*Ber.* vi. 24; *Chem. News*, xxvii. 39) and E. Büchner (*Ber.* vii. 989) were unable to separate nitrogen from ultramarine in weighable quantities, either by heating with acid sodium sulphate in a stream of carbon dioxide, or by fusion with ignited phosphorus salt, or by ignition with soda-lime.

Büchner finds, by experiments in which sodium aluminate was ignited with sulphur and charcoal, with or without silica, that silica is essential to the production of ultramarine. The greater the proportion of silica in the mixture, the smaller is the quantity of sodium sulphate that can be extracted from the product. Büchner is therefore of opinion that the sulphur in ultramarine stands to the silica in closer relation than to the alumina or the soda. Mixtures of clay and sodium carbonate, heated in a stream of hydrogen sulphide or vapour of carbon sulphide, became green and afterwards blue when heated in a current of air. Finely pulverised natrolite, ignited in vapour of carbon sulphide, became black, but on subsequent heating in sulphurous oxide gas it became blue.

On the theory of the formation of Ultramarine, see R. Hoffmann (*Liebig's Annalen*, xciv. 1–22; *Chem. Soc. J.* xxxvi. 108–113).

Crystalline Structure of Ultramarine.—R. Hoffmann first observed that ultramarine possesses a crystalline structure (*Notizen für die Jury der Weltausstellung in Wien*, 1873). This was attributed by Büchner to the presence of crystalline quartz-sand. Grünzweig a. Hoffmann, however, (*Ber.* ix. 864), have confirmed the existence of a crystalline structure in the ultramarine itself, and H. Vogelsang found a preparation received from those chemists to consist for the most part of single-refracting crystals belonging to the regular system. Hoffmann (*Ber.* ix. 868) further observes that these crystals, which have a green colour, are converted by calcination with sulphur into blue ultramarine without alteration of form.

Silver-ultramarine.—K. Heumann (*Ber.* x. 991; *Liebig's Annalen*, cci. 262–291), by acting on ultramarine with solution of silver nitrate, has obtained a yellow amorphous body consisting of a silver-ultramarine, in which one-third of the silver is present as sulphide, and two-thirds as aluminium-silver silicate. According to J. Philipp (*ibid.* 1227), silver nitrate acts both on the ultramarine itself and on the silicates with which it is mixed, producing a mixture of silver ultramarine with several argentiferous silicates. A dilute solution of zinc sulphate acts only on the admixed silicates, but a concentrated solution having a higher boiling temperature acts both on these and on a small portion of the ultramarine itself.

Heumann has obtained potassium, sodium, and lithium ultramarines by fusing silver ultramarine with the iodides of the corresponding metals. The lithium-

Reactions of Ultramarine.

Reagents	Green	Blue (DM)	Violet (VR ₂)	
Dilute mineral acids.	Decomposition .	Decomposition .	Decomposition .	2
Nitric acid in aqueous solution .	"	"	"	3
Oxalic acid in aqueous solution .	Decomposition (H ₂ S)	Decomposition (H ₂ S)	Decomposition (SO ₂) .	4
Concentrated acetic acid .	"	"	"	1
Dilute and cold alum solution .	Decomposition .	"	"	0
Concentrated and slightly warm alum solution .	"	"	"	1
Boiling alum solution .	"	Decomposition .	Decomposition .	1
Cautic solutions, concentrated and dilute, hot and cold .	"	"	"	1
Alkaline solution of lead acetate .	"	"	Turns blue	1
A series of reducing substances (wet way)	"	"	"	1
Ozone .	"	"	"	1
A series of oxidising substances (wet way)	"	"	"	1
Nitric acid silver solution with or without ammonia .	"	"	"	1
Bromine with water and addition of hydrochloric acid .	"	"	"	1
Concentrated nitric acid .	Decomposition. Clay residue .	Bluish-green .	Decomposition. Clay residue .	0
Heated to low redness .	Decomposition .	Decomposition. Clay residue .	Decomposition. Clay residue .	2
A higher temperature .	Bluish-green colour .	Decomposition .	Decomposition .	3
Action of carbonic oxide at high temperatures .	Decoloration .	Decoloration .	Blue colour .	4
Action of hydrogen at high temperatures .	"	"	Decoloration .	4
Action of arsenious acid at high temperatures .	"	"	Blue colour .	3
Action of arsenious acid at a still higher temperature .	Brownish-yellow colour .	"	"	0
Various oxidising substances acting at moderate temperatures (dry way)	"	Green colour .	Green, partly blue .	0
Various oxidising substances acting at high temperatures (dry way)	Blue colour .	"	Light blue .	0
Action of chlorine (dry) at an increased temperature .	Discoloration .	"	Blue colour .	0
Action of chlorine (dry) at a high temperature .	Blue colour .	Decoloration .	Decoloration .	0
Action of alkaline bodies at high temperatures .	Discoloration .	Bluish-violet .	Pink colour .	0
Action of borax at high temperatures .	Decomposition .	Decomposition .	Decomposition .	0
	"	"	Light-blue colour .	0

compound has a fine blue colour, changing to green and afterwards to pink, when the compound is heated with sulphur in a current of air. By heating the blue lithium ultramarine in a current of hydrochloric acid and air, a red compound is formed, which becomes blue on exposure to sulphur vapour or hydrogen.

By long-continued digestion with an ammoniacal solution of silver chloride, blue sodium ultramarine is converted into a yellow compound, in which two-thirds of the sodium in the ultramarine have been replaced by silver. On exposure to hydrochloric acid gas, this product turns blue.

By the action of silver nitrate on green ultramarine at 120°, a yellow compound is obtained, which bears a strong resemblance to the silver ultramarine above described, but differs from it in yielding a green product on fusion with potassium iodide.

Ultramarines containing *alcohol-radicles* are formed by heating silver-ultramarine with alkyl iodides. The *ethyl-compound* is obtained—though not pure—by heating silver-ultramarine with excess of ethyl iodide in a sealed tube at 180° for fifty to sixty hours. It is a light grey or greyish-yellow powder, which when heated gives off ethyl sulphide, together with other products of decomposition, including sulphur dioxide. When, on the other hand, the ethyl-ultramarine is intimately mixed with sodium chloride and very cautiously heated, scarcely any ethyl sulphide is given off, but the mixture, previously grey, turns blue, reproducing ordinary ultramarine. Under these circumstances, ethyl chloride is also given off, the reaction being exactly analogous to the formation of silver chloride when silver-ultramarine is heated with sodium chloride. Similar ultramarines are formed by the action of amyl, allyl, and benzyl iodides; but the two former have not been obtained free from silver (De Forcrand, *Bull. Soc. Chim.* [2], xxxi. 161).

UMBELLIFERONE, or *Hydrozycoumarin*, $C^9H^6O^2 = C^6H^3(OH) \begin{matrix} \diagup CH=CH \\ \diagdown O-CO \end{matrix}$.

This compound is found amongst the products of the dry distillation of the resin of larch-fungus (p. 1165). Its acetyl-derivative, $C^{11}H^7(C^2H^3O)O^2$, or an isomeric thereof, is formed by heating resorcylic aldehyde with sodium acetate and acetic anhydride (p. 1752).

UNDECANE, $C^{11}H^{24}$. This paraffin is formed, together with several of its homologues, lower and higher, by the action of strong sulphuric acid on the products of distillation of the fatty acids (Cahours a. Demarçay). See *HYDROCARBONS* (p. 1064); also by fractional distillation of the product obtained by the action of fuming sulphuric acid on that portion of the spongy mass remaining after the preparation of *cenanthal* from castor-oil, which boils below 200°. Undecane obtained by this latter process boils between 180° and 185° (D. Amato, *Gazz. chim. ital.* 1872, 6).

UNDECOIC ACID, $C^{11}H^{22}O^2 = C^{10}H^{21}.CO^2H$. *Undecylic acid*.—This acid, the eleventh member of the fatty series, is produced by heating undecylenic acid at 200°–220° with hydriodic acid and amorphous phosphorus, and may be purified by treating the crude product with sulphurous acid, then with sodium in alkaline solution; distilling the separated acid under reduced pressure; dissolving the portion which distils at 227°–230° (about 70 per cent.), in alcoholic ammonia; adding an alcoholic solution of lead acetate (which precipitates from 70–80 per cent. of the entire quantity), then adding water, and decomposing the precipitate with nitric acid.

Undecoic acid thus prepared is a colourless scaly mass, transparent immediately after solidification, but quickly exfoliating. It melts at 28.5°, and boils under 160 mm. pressure at 228°. It is insoluble in water, but dissolves very easily in alcohol and in ether. It does not exhibit the indifferent properties of palmitic acid, but on the contrary is somewhat strongly corrosive, and has at ordinary temperatures a not unpleasant odour, recalling that of caproic acid. Bromine acts very slowly on it, and only with the aid of heat.

UNDECOLIC ACID, $C^{11}H^{18}O$ (F. Krafft, *Ber.* xi. 1414). The potassium salt of this acid is obtained by heating dibromundecylenic acid (*infra*) with 2 mol. alcoholic potash in sealed tubes at 180° for three hours; and on decomposing this salt with a mineral acid, undecolic acid separates as a white crystalline precipitate. It melts at 59.5°, may be distilled without change under reduced pressure, dissolves readily in ether, alcohol, and carbon sulphide, very sparingly in water, from which, as well as from dilute alcohol, it crystallises on cooling in thin shining plates. It forms well-defined salts, mostly crystallisable and sparingly soluble. The *barium salt*, $(C^{11}H^{17}O)^2Ba$, forms warty crusts, soluble in 212 pts. water at 15.5°. By fusion with *potash*, undecolic acid is converted into a liquid fatty acid (probably *cenanthylic acid*) boiling at 220°–222°; by *fuming nitric acid* into azelaic acid, $C^9H^{16}O^4$, which may in this way be most conveniently prepared.

UNDECYLENIC ACID, $C^{11}H^{20}O^2$. This acid, which belongs to the acrylic series, was discovered by Krafft, who obtained it, together with cinnamaldehyde, by distilling castor-oil under reduced pressure (p. 1759). It is solid at ordinary temperatures, melts at 24.5° , and boils at 295° with slight decomposition under ordinary pressure, at 200° without decomposition under reduced pressure. Its barium salt crystallises in shining flat needles or plates, sparingly soluble in water, dissolving in 1073 pts. at 15° . When dissolved in carbon sulphide, it readily takes up bromine, forming an addition-product, $C^{11}H^{20}Br^2O^2$, which remains, after evaporation of the solvent, as an unstable crystalline mass, melting at 38° . By fusion with potash, undecylenic acid is converted into acetic acid and nonoic acid, $C^9H^{18}O^2$; by careful heating with nitric acid into sebacic acid (F. Becker, *Ber.* xi. 1412).

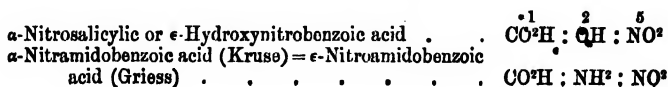
UNONA. The ethereal oil of *Unona odoratissima*, known as a perfume by the name of *Ylang-Ylang*, has been examined by H. Gal (*Pharm. J. Trans.* [3], iv. 28). It has a density of 0.98 at 0.15° ; boils between 160° and 300° ; is optically levogyrate; dissolves completely in ether, partially only in alcohol. From its chemical reactions it appears to be a mixture of benzoic ethers with several alcohols.

URALITE. E. Svedmark (*Jahrb. f. Min.* 1877, 99) has examined the uralite from the uralite-porphyrines of Vaksala near Upsala, from the Ural, from Predazzo, and from Wales, and finds that it is a hornblende produced by metamorphosis of augite.

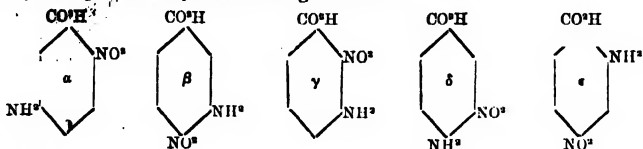
URALIUM. A metal of the platinum group obtained, according to A. Guyard (*Monit. scientif.* 1879, [3], ix. 795), from commercial platinum. In its physical properties it differs but little from pure platinum. It is the whitest of all metals except silver, as extensible as platinum, and much more flexible; melts only at very high temperatures, but probably somewhat lower than pure platinum. Sp. gr. = 20.25 at 15° . Atomic weight 187.25—187.50. It resembles platinum also in its chemical reactions. The double chloride of lithium and uralium is somewhat less soluble in absolute alcohol than that of potassium and platinum. Uralium is distinguished from platinum chiefly by its behaviour towards potassium cyanide. When platinum chloride [from commercial platinum] and potassium cyanide are fused together, reduced platinum is obtained, together with a reddish-yellow melt, the colour of which is due to uralium cyanide. If the platinum thus reduced be reconverted into chloride and fused with potassium cyanide, the melt becomes continually lighter in colour the oftener the process is repeated; whereas, if the metals be again separated from the coloured melt, then reconverted into chlorides and fused with potassium cyanide, the melt becomes continually darker in colour, in consequence of the uralium accumulating therein. By repeating this process several times, Guyard obtained from 2 kg. platinum about 2 g. nearly pure uralium.

URAMIDOBENZOIC ACID, $C^6H^5N^2O^3 = C^6H^4 \begin{matrix} \text{NH.CO.NH}^2 \\ \text{CO.OH} \end{matrix}$. The meta-modification of this acid distilled with a fourth of its weight of phosphoric anhydride, yields a considerable quantity of metacyananiline (m. p. 54°). Para-uramidobenzoic acid treated in like manner yields small quantities of paracyananiline melting at 86° (Griess, *Ber.* viii. 224).

Ortho-uramidobenzoic or Uramidosalicylic Acid, $[COOH : NH.CO.NH^2 = 1 : 2]$ (Griess, *Ber.* xi. 1729). This acid, like the para-modification (uramidodraeylic acid, vii. 166), yields, when treated with nitric acid, only one dinitro-uramidobenzoic acid, which closely resembles its isomeride obtained from meta-uramidobenzoic acid (vii. 167). By boiling with water this dinitro-acid is converted into ϵ -nitramidobenzoic acid, identical with that already described (p. 1462) as obtained by the action of alcoholic ammonia on diethyl α -nitrosalicylate. The ϵ -hydroxynitrobenzoic acid obtained by boiling this nitroamido-acid with potash-ley is likewise identical with ordinary or α -nitrosalicylic acid melting at 228° . By reduction with tin and hydrochloric acid, the ϵ -acid is converted into α -diamidobenzoic acid, $[CO^2H : NH^2 : NH^2 = 1 : 2 : 5]$ (p. 273), analogous to *p*-phenylenediamine, and derived from *o*-amidobenzoic acid. Hence the compounds above mentioned may be represented by the following formulae:



The whole of the nitroamid-acids obtained by Griess from the uramidobenzoic acids may be represented by the following formulæ:



URAMIDOCAPROIC ACID, $C^7H^{14}N^2O^3 = NH^2.CO.NH.C^5H^{10}.COOH$. This acid appears to be identical in composition with a compound, crystallising in needles, which is obtained by fusing leucine with urea (F. Hofmeister, *Ber.* vi. 1278).

URAMIDOISETHIONIC ACID, $C^7H^8N^2SO^4 = NH^2.CO.NH.C^2H^4.SO^3H$. Syn. with TAUCROCARBAMIC ACID (p. 1892).

URAMIDOISOBUTYRIC or **ACETONYLURAMIC ACID**, $NH^2.CO.NH.C(CH^3)^2.COOH$. See ACETONYL-UREA (vii. 18).

URANIUM. *Atomic Weight.*—J. Donath (*Wien. Acad. Ber.* [2 Abth.], lxxix. April-heft) has determined the specific heat of uranoso-uranic oxide by means of Bunsen's ice-calorimeter (vii. 595), and finds it to be equal to 0.07979. Hence, assuming the specific heat of oxygen in solid compounds to be 0.25, that of metallic uranium must be 0.0421, a value which, when multiplied by the old atomic weight of uranium, 120, gives for the atomic heat the value 5.04, agreeing with the average atomic heat of the metals (^e) much more nearly than the number 10.08 obtained with Mendelejeff's value (240) of the atomic weight of uranium. As, however, the matter cannot be regarded as quite decided, and there are many considerations which favour the adoption of the higher atomic weight, the uranium compounds about to be described will be represented by formulæ in accordance with it (compare vii. 1189).

The presence of Uranium in the sun has been demonstrated by Lockyer (*Proc. Roy. Soc.* xxvii. 279).

On the Fluorescence, Phosphorescence, and Absorption-spectra of Uranium-compounds, see LIGHT (p. 1195).

A process for the preparation of pure uranium-compounds, with especial attention to the separation of Vanadium, is described by C. Bolton (*Amer. Chem.* v. 363).

A method of separating uranium from the residues obtained in the titration of phosphoric acid (p. 1584) depending on the solubility of uranic phosphate in ammonium carbonate, and the complete precipitation of the phosphoric acid from the resulting solution by magnesia-mixture, is described by A. Gawalowski (*Zeitschr. anal. Chem.* 1876, 292; *Chem. Soc. J.* 31, 345). Another method is given by H. Strohmer (*Dingl. pol. J.* ccxxv. 56; *Chem. Soc. J.* xxxiv. 115).

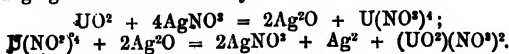
• *Separation of Uranium from Iron and Chromium.*—A. Ditte (*Compt. rend.* lxxxv. 281) effects this separation for quantitative analysis by precipitating the oxides with ammonia; igniting the dried precipitate in a stream of hydrogen; weighing the residue and igniting it in a stream of hydrogen chloride to distil off the iron as ferrous chloride; extracting the uranous oxide (UO^2) from the weighed residue by nitric acid; and finally igniting the undissolved portion, and weighing it as chromic oxide.

The method of igniting the unprecipitated oxides in hydrogen, and distilling off the iron as chloride in a stream of hydrogen chloride, may of course be employed also for the separation of uranium from iron alone.

On the separation of Uranium from Chromium, see also CHROMIUM (p. 457).

A Chemico-technological report on Uranium-compounds is given by A. Patera in Hofmann's *Entwicklung der chemischen Industrie*, p. 986.

OXIDES AND SALTS OF URANIUM.—1. **Dioxide or Uranous oxide**, UO^2 . A hydrate of this oxide is obtained by the action of hydrogen dioxide on uranium nitrate, as a yellowish-white precipitate, which, when dried at 100° , has the composition $UO^2.H^2O$ (T. Fairley, *Chem. Soc. J.* xxxii. 319). When uranous oxide is added to a solution of silver nitrate, a precipitate of metallic silver is formed, the reaction, according to Isambert (*Compt. rend.* lxxx. 1087), taking place by two stages, an argentous and a uranous salt being formed in the first instance, and the argentous oxide being afterwards reduced, with formation of a uranyl salt, the green colour of the liquid changing at the same time to yellow:



The oxide U^2O^3 also throws down metallic silver from a solution of the nitrate, though very slowly.

Uranic Oxide and Uranyl-compounds (R. Sendtner, *Liebigs Annalen*, xciv. 325).

Uranyl Selenates are obtained by dissolving uranoso-uranic oxide in dilute selenic acid, and evaporating the solution on the water-bath. The strongly acid concentrated liquid deposits, after some time, light yellow, tough, very deliquescent masses, having a wavelitic structure, and agreeing approximately in composition with the formula $(\text{UO}^2)\text{SeO}^4, \text{H}^2\text{SeO}^4 + 18\text{H}^2\text{O}$. At the same time there is formed another salt, $2(\text{UO}^2)\text{SeO}^4, \text{H}^2\text{SO}^4 + 12\text{H}^2\text{O}$, which is more permanent in the air, and crystallises more readily in greenish-yellow needles, which are difficult to dry, and easily effloresce. A saturated solution of uranic-hydroxide in selenic acid dries up in the exsiccator to a varnish-like mass.

Uranyl-potassium Selenate, $(\text{UO}^2)\text{SeO}^4, \text{K}^2\text{SeO}^4 + 2\text{H}^2\text{O}$, is obtained by mixing a solution of uranic oxide in selenic acid containing the smallest possible quantity of free acid, with potassium selenate, and evaporating to the crystallising point, or better by adding potassium uranate to warm selenic acid as long as it continues to dissolve. The double salt crystallises from aqueous solution in granular crusts. *Uranyl-ammonium Selenate*, $(\text{UO}^2)\text{SeO}^4, (\text{NH}^4)^2\text{SeO}^4 + 2\text{H}^2\text{O}$, prepared in like manner, is very soluble in water.

Selenites.—*Uranyl-hydrogen Selenite*, $(\text{UO}^2)\text{SeO}^3, \text{H}^2\text{SeO}^3$, noticed by Berzelius (v. 229), may be prepared by adding uranic hydroxide to boiling selenious acid, whereupon a violent reaction takes place, and the hydroxide is converted into a lemon-yellow crystalline powder. The same compound is more abundantly produced by mixing uranyl chloride with selenious acid, and heating the mixture to boiling, whereupon it deposits a large quantity of the acid salt in yellow microscopic crystals.

Uranyl-potassium Selenite, $(\text{UO}^2)\text{SeO}^3, \text{K}^2\text{SeO}^3$, is obtained in greyish-yellow crystalline crusts insoluble in water, on saturating warm selenious acid with potassium uranate. The *ammonium salt*, $(\text{UO}^2)\text{SeO}^3, (\text{NH}^4)^2\text{SeO}^3$, prepared in like manner, forms microscopic crystals of a deeper yellow colour and likewise insoluble in water.

Uranyl Bromide, $\text{UO}^2\text{Br}^2 + 7\text{H}^2\text{O}$, is obtained, as already described (v. 942), by dissolving uranic hydroxide in strong hydrobromic acid, as a yellowish-brown mass which deliquesces on exposure to the air, and unites very readily with other metallic bromides, forming double salts which are most easily obtained by dissolving the corresponding uranates in hydrobromic acid. The *potassium salt*, $\text{UO}^2\text{Br}^2, 2\text{KBr} + 7\text{H}^2\text{O}$, crystallises in yellow-brown rhombic plates, which dissolve very readily in water but are decomposed thereby. The *ammonium salt*, $\text{UO}^2\text{Br}^2, 2\text{NH}^4\text{Br} + \text{H}^2\text{O}$, forms large rhombic plates, somewhat less stable than the potassium salt, but very much like it in other respects (Sendtner).

Uranic hydroxide dissolves in *hydriodic acid*, forming a dark-brown liquid, solidifying in the exsiccator to a brown-black mass which gives up free iodine, and after the removal of this body, yields nothing but the uranium iodide described by Rammelsberg (v. 945).

Tetroxide, UO^4 (T. Fairley, *Chem. Soc. J.* 1877, xxxi. 127). When hydrogen dioxide is added to a solution of uranyl nitrate or acetate, a yellowish-white precipitate is formed, which in presence of an excess of the uranyl salt is very stable, and may be dried without deposition even at 100° . The precipitation is prevented by the presence of salts of the alkali-metals, or of barium or calcium salts, as well as by a moderate excess of a strong mineral acid, especially sulphuric acid. The dried precipitate is a yellowish-white powder, dissolving in strong hydrochloric acid, with evolution of chlorine. When heated to a temperature somewhat below redness, it burns away with a glimmering light, giving off oxygen and leaving green uranic oxide. On treating it with alkalis, part of it is precipitated as uranic oxide, while another portion dissolves in combination with the alkali, forming a salt of peruranic acid, an acid analogous in composition to perchromic acid (i. 953). The composition of the air-dried compound is $\text{UO}^4, 6\text{H}^2\text{O}$; that of the compound dried at 100° is $\text{UO}^4, 2\text{H}^2\text{O}$. The mode of decomposition of this compound by alkalis, however, tends to show that its molecular weight is three times as great as that which is denoted by the latter formula, and that it must be regarded as a uranic salt of peruranic acid, $\text{UO}^4, 2\text{UO}^3 + 6\text{H}^2\text{O}$. The anhydrous tetroxide appears to be formed when the hydrogen dioxide is added to a large excess of uranic nitrate solution. In this case no precipitate is formed at first, and it is only after some weeks that a heavy white crystalline precipitate is deposited, having the empirical composition UO^4 . Higher oxides have not been obtained in the free state, but free peruranic acid, $\text{UO}^4, 2\text{H}^2\text{O}$, appears to exist in the precipitates which are formed by the slow decomposition of its salts.

Ammonium Peruranate, $\text{UO}^4, \text{UO}^3, (\text{NH}^4)^2\text{O} + 8\text{H}^2\text{O}$ or $2\text{UO}^4, (\text{NH}^4)^2\text{O}^2 + 8\text{H}^2\text{O}$, is thrown down on addition of alcohol to a solution of uranic nitrate mixed with hydrogen dioxide and excess of ammonia, as an orange-yellow precipitate easily soluble in

water and less alterable in contact with the air than the corresponding sodium or potassium salt. When alkaline hydroxides are added to a solution of this ammonium salt, uranic hydroxide is precipitated and peruranates are dissolved. Its solution gives precipitates with most metallic salts. The salt when heated smoulders away like tinder, and leaves a residue consisting of lower oxides of uranium.

Sodium Peruranate, $\text{UO}^6_2\cdot 2\text{Na}^2\text{O} + 8\text{H}^2\text{O}$ or $\text{UO}^4_2\cdot \text{Na}^4\text{O}^4 + 8\text{H}^2\text{O}$, is readily obtained by dissolving ordinary uranic hydroxide or the hydrate of the above-mentioned tetroxide in soda-ley, with addition of hydrogen dioxide. If the solutions are sufficiently concentrated, the sodium salt separates after a few seconds in yellow needles often united in stellate groups; if they are dilute, the separation may be effected by addition of a little alcohol. The crystals have a golden lustre when freshly prepared, but effloresce on exposure to the air, taking up carbon dioxide, and giving off oxygen. The salt forms precipitates with most metallic salts. When heated alone it gives off three-fourths of its water and 3 at. oxygen; when heated in a stream of carbon dioxide it gives off all its water. *Red sodium peruranate*, $\text{UO}^6_2\cdot \text{UO}^4_2\cdot \text{Na}^2\text{O} + 6\text{H}^2\text{O}$ or $2\text{UO}^4_2\cdot \text{Na}^2\text{O}^2 + 6\text{H}^2\text{O}$, is formed when the minimum quantity of caustic soda is used, and separates on addition of alcohol, before the former salt, in the form of a deep-red oil, which slowly becomes crystalline.

Potassium Peruranate, $\text{UO}^6_2\cdot 2\text{K}^2\text{O} + 10\text{H}^2\text{O}$ or $\text{UO}^4_2\cdot \text{K}^4\text{O}^4 + 10\text{H}^2\text{O}$, prepared like the corresponding sodium salt, is a yellow-red or orange-red precipitate; it is even more unstable than the sodium salt, and rapidly absorbs carbonic acid from the air (Fairley).

URANOSPHERITE, $\text{Bi}^2\text{O}^3\cdot \text{UO}^3_2 + \text{H}^2\text{O}$, and **URANOSPINITE** $\text{CaO}_2\cdot 2\text{UO}^3_2\cdot \text{As}^2\text{O}^3 + 8\text{H}^2\text{O}$. See URANIC ARSENATES (vii. 1190).

UREAS. See CARBAMIDES (pp. 388–401).

URECHITIS. The leaves of *Urechitis suberecta*, a poisonous plant growing in Jamaica, sometimes in clumps, but more frequently, as a creeper, yield three active principles, which have been examined by J. Bowrey (*Chem. Soc. J.* xxxiii. 252), and are named by him *Urechitin*, *Crystallised Urechitoxin*, and *Amorphous Urechitoxin*; neither of them contains nitrogen.

Urechitin, $\text{C}^{28}\text{H}^{42}\text{O}^8$, obtained from the air-dried leaves by extraction with alcohol, crystallises in colourless hydrated needles, nearly insoluble in water and dilute alcohol, more readily soluble in ether, hot alcohol, amyl alcohol, chloroform, and glacial acetic acid. By strong acids it is decomposed like a glucoside. Strong sulphuric acid dissolves it, forming a yellow liquid, which gradually turns red and finally purple, the change of colour being accelerated by the addition of a trace of any oxidising substance. *Urechitin* is intensely bitter (even to the 40,000th degree of dilution) and very poisonous.

Crystalline urechitoxin, $\text{C}^{13}\text{H}^{20}\text{O}^5$, extracted from the leaves after drying at 100° , is more readily soluble than *urechitin*. It is bitter, poisonous, easily alterable, and is resolved by acids into *urechitoxetin*, and a substance which reduces cupric oxide. *Amorphous urechitoxin* resembles the crystallised modification, but has not yet been obtained pure.

The leaves of *Urechitis* are intensely bitter and very acid, and produce on the lips and tongue a sensation of being swollen and blistered; their powder applied to the nostrils produces violent sneezing. These active properties are possessed by all the green parts of the plant, and by the flowers, but exist very slightly, if at all, in the woody portions. The poisonous action is due to the presence of *urechitin*, the decomposition of which gives rise to *urechitoxin*.

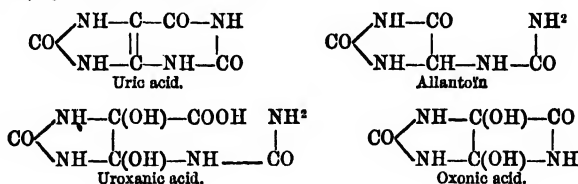
URETHANES. See CARBAMATES, ALCOHOLIC (p. 384).

URIC ACID, $\text{C}^5\text{H}^4\text{N}^4\text{O}^3$. *Formation from Ammonia in the Animal Organism*. From experiments by W. Schröder (*Zeitschr. physiol. Chem.* ii. 228) it appears that ammonia, when introduced by the mouth into the bodies of poultry, in combination with carbonic acid, or with any organic acid that is easily oxidised in the circulation to carbonic acid and water, is for the most part converted into uric acid.

Oxidation.—1. When *iodine* is added to uric acid suspended in water, the uric acid disappears gradually, or more quickly on application of heat, and *alloxan* is found amongst the products, together with hydriodic acid and apparently also *urea* (F. Wurtz, *Compt. rend.* lxxvii. 1548). 2. When *bromine* is dropped into water in which uric acid is suspended, the latter is oxidised to *isalloxanic acid*, $\text{C}^4\text{H}^4\text{N}^4\text{O}^3$ (Magnier de la Source, p. 1127). 3. Uric acid, exposed in alkaline solution to the action of *atmospheric oxygen*, is converted into *oxonic acid*, $\text{C}^4\text{H}^4\text{N}^4\text{O}^4$ (Strecker, p. 1458). 4. Uric acid, treated in alkaline solution with the exact quantity of *potassium permanganate* required for its oxidation, yields *allantoïn* in nearly

theoretical quantity. When the action takes place in the cold, 1 mol. permanganate oxidises 3 mol. uric acid, or 1 mol. uric acid takes up 3 at. oxygen. To ensure the quantitative fulfilment of the reaction, all rise of temperature must be avoided, and as soon as the colour of the permanganate has disappeared, the liquid must be filtered from the deposited manganese dioxide and supersaturated with acetic acid. The colourless liquid free from manganese, if left to itself in the cold for twenty-four hours, deposits the allantoin produced by the reaction (A. Claus, *Ber.* vii. 226). 5. By the action of *ammonium cuprate* in presence of potash, uric acid is resolved into urea and oxalic acid (O. Loew, *J. pr. Chem.* [2], xviii. 298).

The relation between uric acid and certain of its oxidation-products, which by their decomposition yield glyoxalyl-urea, may be represented according to L. Medicus (*Ber.* x. 544) by the following formulæ

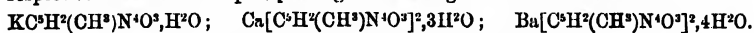


Estimation.—To estimate uric acid in urine, E. Salkowsky (*Zeitschr. anal. Chem.* 1877, 371) mixes 200 c.c. of the urine with an alkaline carbonate to strong alkaline reaction; adds after an hour 20 c.c. of strong sal ammoniac solution; and leaves the liquid to itself for forty-eight hours in a cool place. The precipitate having been washed two or three times on a weighed filter, this filter is filled with dilute hydrochloric acid; the liquid which runs through is collected, this treatment being repeated till the ammonium urate is completely converted into uric acid; and the filtrate is left to itself for six hours. The uric acid thus separated is added to the portion first precipitated, and the whole is twice washed with water, then with alcohol till the filtrate appears neutral, and dried at 110°. To the weight thus obtained it is necessary to add 0.030 (the weight of uric acid dissolved in 200 c.c. water). Thin urines must be evaporated down till they exhibit a specific gravity of 1.017–1.020.

On the Estimation of Uric acid in Urine, see also R. Maly (*Liebig's Annalen*, clxv. 315; *Jahresb. f. Chem.* 1873, 980; and Magnier de la Source, *Bull. Soc. Chim.* [2], xxi. 290; *Jahresb.* 1874, 1052).

Methyluric Acid, $\text{C}^5\text{H}^2(\text{CH}^3)\text{N}^4\text{O}^3$, is obtained by heating dry lead urate to 150°–160° with methyl iodide diluted with ether, and treating the product with hydrogen sulphide to remove lead. The hot filtrate, on cooling, deposits crystals of methyluric acid, which are purified by dissolving them in hot soda-ley, precipitating with hydrochloric acid, and recrystallising from boiling water. It forms thin prisms, fusible with decomposition at a high temperature, soluble in 250 pts. of boiling water, nearly insoluble in alcohol and ether. The aqueous solution reddens litmus. The ether dissolves in cold strong sulphuric acid, and is deposited in crystals when the solution is diluted. It dissolves easily in alkalis: alcohol throws down from the solutions dense precipitates of the alkali-salts, aqueous solutions of which precipitate many salts of the metals.

Alcohol added to a solution of the acid in potash throws down the salt $\text{K}^2\text{C}^5\text{H}(\text{CH}^3)\text{N}^4\text{O}^3 + 3\text{H}^2\text{O}$, and the corresponding sodium salt is obtained in like manner. A solution of the acid in hot baryta-water deposits on cooling tufts of delicate needles of the barium-salt, $\text{BaC}^5\text{H}(\text{CH}^3)\text{N}^4\text{O}^3 + 3\frac{1}{2}\text{H}^2\text{O}$, and a similar salt is formed with calcium hydrate. The following salts are formed by boiling the acid with the respective carbonates and precipitating the resulting solutions with alcohol:—



A solution of the mono-barium salt mixed with sodium sulphate gives, on addition of alcohol, a precipitate of the salt, $\text{NaC}^5\text{H}^2(\text{CH}^3)\text{N}^4\text{O}^3, \text{H}^2\text{O}$. Moderately strong solutions of the alkali salts gelatinise on cooling.

Methyluric acid in alkaline solution, when oxidised with a dilute solution of potassium permanganate, yields methylallantoin, $\text{C}^5\text{H}^3(\text{CH}^3)\text{N}^4\text{O}^3$, which substance crystallises in monoclinic prisms resembling allantoin, and melts with decomposition at 225°. A silver compound, $\text{AgC}^5\text{H}^4(\text{CH}^3)\text{N}^4\text{O}^3$, is formed on adding silver nitrate and excess of ammonia to a hot solution of methylallantoin: it crystallises in short prisms soluble in hot water. Methylallantoin, heated with strong hydriodic acid, yields urea and methylhydantoin—



Methyluric acid is oxidised by potassium chlorate and hydrochloric acid in the manner indicated by the following equation, the products being urea and methylalloxan:—



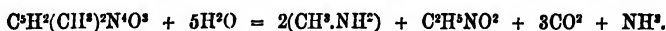
Methylalloxan, boiled with strong nitric acid, yields methyl-parabanic acid, $C^4H(CH^3)N^2O^3$ (H. Hill, *Ber.* ix. 370, 1090; *Sill. Am. J.* [3], xii. 428).

Dimethyluric Acid, $C^6H^2(CH^3)^2N^4O^3$ (Mabery a. Hill, *Ber.* xi. 1329). This acid is best prepared by heating lead urate with a slight excess of methyl iodide diluted with an equal quantity of ether. The decomposition proceeds rapidly at 165°, and is completed in fifteen to twenty hours. The product of the reaction is boiled with water, the dissolved lead removed by sulphuretted hydrogen, and the crystals which separate out on cooling are recrystallised from hot water.

Dimethyluric acid forms small monoclinic prisms containing 1 mol. of water. From saturated solutions it sometimes separates at temperatures near 100° in thick prisms, pointed at both ends and anhydrous. It melts only at a high temperature, with partial decomposition and sublimation; dissolves in 200 pts. of boiling and 800 pts. of cold water, scarcely at all in alcohol, ether, and glacial acetic acid, easily in concentrated sulphuric and hydrochloric acids, and crystallises out on dilution.

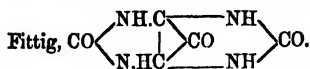
Dimethyluric acid is bibasic. The *dipotassic salt*, $K^2C^6H^2(CH^3)^2N^4O^3 + 4H^2O$, is formed on dissolving the acid in a small quantity of hot potash-ley, and separates, on addition of alcohol, in silky needles very soluble in water, very slightly soluble in alcohol. The *disodic salt*, $Na^2C^6H^2(CH^3)^2N^4O^3 + 4\frac{1}{2}H^2O$, obtained in like manner, is still less soluble in alcohol. The *acid salts*, $KC^6H^2(CH^3)^2N^4O^3 + 1\frac{1}{2}H^2O$, and $NaC^6H^2(CH^3)^2N^4O^3 + 2\frac{1}{2}H^2O$, are obtained by boiling the acid with aqueous potassium or sodium carbonate, and precipitating with alcohol. The *normal barium salt*, $BaC^6H^2(CH^3)^2N^4O^3 + 3H^2O$, obtained by dissolving the acid in baryta-water, separates on cooling in flat transparent prisms, soluble with difficulty in cold water, more easily in hot. The *acid salt*, $Ba[C^6H^2(CH^3)^2N^4O^3]^2 + 3H^2O$, is obtained by boiling an aqueous solution of the acid with barium carbonate, and precipitating with alcohol.

Dimethyluric acid heated to 170° with strong hydrochloric acid is resolved into carbon dioxide, ammonia, methylamine, and glycocine, according to the equation

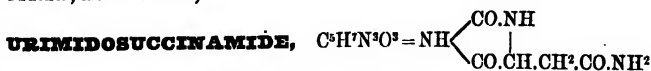


The preceding facts show that the two hydrogen-atoms in uric acid which are replaceable by metals are directly combined with two distinct nitrogen-atoms. If these two hydrogen-atoms be replaced by methyl, the two remaining hydrogen-atoms may then be exchanged for metals. This relationship finds a simple explanation only on the assumption that uric acid contains the group NH four times; and this requirement is fulfilled by two only of the various structural formulæ proposed

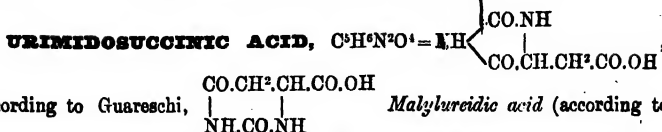
for uric acid, viz., by that of Medicus, $\begin{matrix} NH.CO.C.NH \\ || \\ CO.NH.C.NH \end{matrix} \rangle CO$ (p. 2076), and by that of



Isouric Acid, $C^6H^4N^4O^3$ (perhaps = $CO \langle \begin{matrix} NH & - & CO \\ NH & - & CO \end{matrix} \rangle CH-N=C=NH$), is formed by mixing a concentrated boiling solution of alloxantin with a solution of cyanamide, and separates on boiling the mixture briskly as a heavy powder. Its solution in dilute potash-ley gives with excess of hydrochloric acid a gelatinous precipitate which, unlike that of uric acid, does not become crystalline when heated with hydrochloric acid. The same solution, like that of uric acid, gives with silver nitrate an immediate black precipitate. Isouric acid further resembles uric acid in being nearly insoluble in water and in exhibiting a faint acid reaction after boiling therewith (E. Mulder, *Ber.* vi. 1233).



(Guareschi, *Gazz. chim. ital.* 1876, 370). This substance, identical with Grimaux's *Methyluramide* (*Compt. rend.* lxxi. 325), is formed by the action of urea on asparagine. It crystallises with great facility, melts with decomposition at 230°–235° is insoluble in cold water, also in alcohol and in ether.



according to Guareschi, $\left| \begin{array}{c} \text{CO.CH}^2\text{CH.CO.OH} \\ \text{NH.CO.NH} \end{array} \right|$ *Malyureidic acid* (according to Grimaux)

is formed by heating the amide just described with acids (Guareschi), also by heating aspartic acid (2 pts.) with urea (1 pt.) at 125° – 130° for eight hours (Grimaux). The solution of its ammonium salt gives with ferric chloride and a little ammonia a brown precipitate slightly soluble in acetic acid. The *silver salt* remains unaltered at 100° – 110° . The *barium salt*, $(\text{C}^8\text{H}^8\text{N}^2\text{O}^4)^2\text{Ba} + 4\text{H}_2\text{O}$, gives off its water at 100° – 120° (Guareschi); according to Grimaux, the air-dried salt contains 1 mol. H_2O . The acid treated with fuming nitric acid is converted into a crystalline body which is coloured yellow by alkalis, and decomposes with explosive violence when heated to 188° (Guareschi).

URINE. Constituents.—1. Thiocyanates. J. Munk (*Ber.* ix. 1799) observes that when the urine of men or dogs is distilled with hydrochloric or sulphuric acid, hydrogen sulphide and hydrogen cyanide may be detected in the distillate, and he attributes these products to the decomposition of a thiocyanate contained in the urine. By a quantitative estimation in the form of silver thiocyanate, he finds that 100 c.c. urine contains on the average 0.008 g. thiocyanic acid. The existence of thiocyanates in the urine of men, horses, oxen, rabbits, dogs, and cats has also been demonstrated by Gscheidlen (*Chem. Centr.* 1877, 88; *Jahresb. f. Chem.* 1877, 1001; *Chem. Soc. J.* xxxii, 205).

2. Acid Sulphuric Ethers are found in the urine of various animals. The amount of these ethers is considerable in the urine of herbivora, and in that of the horse it exceeds the quantity of sulphuric acid present as sulphates. The same ethers are normal constituents of man's and dog's urine, in which, however, they exist in much smaller quantities. The three principal sulphuric ethers of urine are the so-called 'phenol-forming,' 'indigo-forming,' and 'catechol-forming' substances, the last of which is found only in horse's urine.

The phenol-forming substance may be obtained in the crystalline state by simply evaporating horse's urine to a syrup, treating this with alcohol, and evaporating the alcoholic liquid to a thin syrup, which is left for some days in the cold. A brown crystalline mass is thus obtained, which, after recrystallisation from water, forms dazzling-white pearly plates, solutions of which exhibit a fine blue fluorescence. The crystals may be boiled with acetic acid without decomposition; when heated with strong hydrochloric acid they break up into phenol and acid potassium sulphate. They yield on analysis numbers agreeing with the formula of potassium phenylsulphate.

The urine of patients under treatment with phenol contains no trace of that substance in the free state, but after being warmed with hydrochloric acid, it yields considerable quantities of phenol. Such urine always contains a large proportion of acid sulphuric ethers, amounting to ten to fifteen times the quantity present in normal human urine.

Direct experiments with dogs showed that, after the introduction of phenol in sufficient quantity into the system, sulphates almost entirely disappeared from the urine, their place being taken by phenylsulphates. The urine contained only a trace of phenol, but much phenylsulphuric acid. Analogous results were produced by the administration of catechol. (E. Baumann, *Ber.* ix. 54; *Pflüger's Archiv. f. Physiologie*, xii. 691; xiii. 285).

Cresols (*o*-, *m*-, and *p*-) are found in horse-urine as cresyl-sulphuric acids (Priesse, *Zeitschr. Physiol. Chem.* ii. 355).

3. Inosite. From experiments made by E. Külz on six persons, it appears that inosite occurs in the urine of healthy individuals after drinking large quantities of water. The occurrence of inosite in diabetes insipidus is not constant.

4. Allantoïn has been found in the urine of a dog fed on meat and fat. Hippuric acid also is found in small quantity in the urine of dogs fed on meat, the maximum amount being 1 pt. hippuric acid to 129 pts. urea (E. Salkowski, *Ber.* xi. 500).

5. Oxalates. From examination of forty-four specimens of urine, A. B. Prescott (*Chem. News*, xxxvii. 76) finds that urine which in the fresh state is free from calcium oxalate, frequently deposits oxalates after standing for five days.

Relative Weight of different Constituents of Urine.—The urine of a dog fed on meat alone was found to contain 14 pts. by weight of phosphoric acid to 100 nitrogen; that of a dog fed on potatoes and bread contained 20 to 30 phosphoric acid to 100

nitrogen. In healthy men from twenty to twenty-five years old, living on a sufficiency of mixed diet, the urine contains from 17 to 19 pts. phosphoric acid to 100 nitrogen; with pure meat diet the phosphoric acid decreases; with pure vegetable diet it increases. The proportion of the two constituents varies greatly also with the time of day and the state of health. The urine of healthy men contains to 100 pts. nitrogen, 12 to 14 sulphuric acid, 0.3 to 0.7 lime, and 0.6 to 1.0 magnesia (W. Zuelzer, *Ber.* viii. 1670).

Influence of various Substances on the Composition and Properties of the Urine.—

1. Benzoic acid. The urine of a dog whose food was mixed with benzoic acid was found by Baumstark (*Ber.* vi. 883) to contain a substance having the composition $C^9H^9N^2O$. This substance unites with acids, forming easily soluble salts; is precipitated by mercuric nitrate; yields sarcosolactic acid when treated with nitrous acid; and gives off half its nitrogen as ammonia when boiled with baryta-water, the other half probably as ethylamine, with separation of barium carbonate.

2. Orthonitrotoluene. This substance given to dogs in their food appears in the urine, partly as orthonitrobenzoic acid, but the chief product of its transformation is a crystalline substance having the composition $C^{14}H^{10}N^3O^{10} + 2\frac{1}{2}H^2O$, which may be regarded as a compound of urea with *uronitrotoluenic acid*, $C^{12}H^{12}NO^9$ (Jaffé; see p. 1994).

3. Salicylic acid. Sodium salicylate, introduced into the stomach of a dog, appears in the urine after forty-five minutes. In man it is quickly eliminated by the kidneys, appearing in the urine after twenty minutes (Blanchier a. Bochefontaine, *Compt. rend.* lxxvii. 657).

4. Salicin, taken by the mouth, passes into the urine partly unaltered, partly decomposed, with formation of salicylic acid (Weith, *Ber.* x. 979).

5. Proteids. Many of these bodies, when introduced into the animal body by intravenous injection, remain there: others are eliminated in the urine, either unaltered or after undergoing various transformations. The urine after such injections is mostly alkaline (Béchamp a. Batus, *Ann. Chim. Phys.* [5], xiv. 512).

6. When urine voided after eating asparagus is distilled, an alkaline distillate is obtained having the characteristic odour of asparagus. Such urine contains a proportion of ammonia much above the normal amount; considerable quantities of succinic acid; also hippuric and benzoic acids, but no asparagine. This last substance must therefore have been decomposed, in passing through the organism, into succinic acid and ammonia, which appear in the urine (A. Hilger, *Liebig's Annalen*, clxxi. 308).

7. On the influence of Chloral Hydrate on the composition of the Urine, see UROCHLORALIC ACID (p. 2080).

Pathological Urine.—Markownikoff (*Ber.* ix. 1441, 1603) has found acetone and ethyl alcohol in *diabetic urine*, and is of opinion that these bodies are formed in the organism by a peculiar fermentation of glucose induced by an *acetone-ferment*. E. Reichardt found dextrin in the urine of diabetic patients who had been drinking the Carlsbad waters (*Arch. Pharm.* [3], v. 502). The urine of a *typhus patient* was found by A. Strumpell (*Zeitschr. anal. Chem.* xvi. 134) to contain thiosulphuric acid. Selmi (*Ber.* vii. 1463) finds that fresh urine voided after poisoning with phosphorus does not give off phosphine when treated with zinc and sulphuric acid, but that, after standing for twenty-four hours, it acquires an alliaceous odour, and then gives off phosphine when treated as above.

On the colouring matters obtained from the urine of a leprous patient, see UROSCOPHÆMATIN (p. 2080).

Detection and Estimation of various Substances in Urine.—1. Albumin. See PROTEIDS (p. 389). 2. Blood (p. 387). 3. Indigo. To estimate this substance, E. Salkowski (*Zeitschr. anal. Chem.* 1877, 366), after oxidising the urine, renders it alkaline with caustic soda, whereby the indigo is precipitated together with phosphates, and extracts the indigo from the dried precipitate with chloroform. 4. Iodine may be estimated by acidulating the urine with hydrochloric acid, and titrating with a solution of palladium chloride, 10 c.c. of which are equivalent to 0.0119 g. iodine. The titration is best performed by measuring out 10 to 20 c.c. of the palladium solution, heating the liquid in a stoppered flask placed in the water-bath, and adding the urine-solution, previously brought to a definite volume, till all the palladium is thrown down as PdI^2 (A. Hilger, *Zeitschr.* 1873, 342; *Liebig's Annalen*, clxxi. 212). 5. Peptone. See PROTEIDS (p. 1689). 6. Phenol may be detected by agitating the urine with petroleum-ether, which dissolves the phenol; and testing the solution with ferric chloride, bromine-water, chloride of lime with ammonia, mercuric nitrate with a small quantity of nitrous acid (Dragendorff, *Arch. Pharm.* [3], xii. 298).

7. Quinine may be detected by rendering the urine alkaline with ammonia, agitating with ether, which takes up the quinine, evaporating after addition of hydrochloric acid, and testing with chlorine-water, which, if quinine is present, brings out the well-known green coloration (Vitali, *Zeitschr. anal. Chem.* 1874, 476). 8. Urea. See CARBAMIDES (p. 389). 9. Uric acid (p. 2076).

URN-RESIN. This resin, which is of frequent occurrence in ancient tombs, has been examined by Hostman & Flückiger (*Arch. Pharm.* [3], vii. 1). It consists of a dark-coloured amorphous mass, which softens at 100° without melting, and gives off an odour like that of storax. It burns with a smoky flame, leaving 1.58–1.66 per cent. ash, which does not effervesce with hydrochloric acid, has an alkaline reaction, and contains manganese. Petroleum-ether and alcohol dissolve but little of the resin, carbon sulphide rather more; ether takes up about 60 per cent. of it. The resin extracted by ether gave by combustion 72.77 per cent. carbon and 9.26 hydrogen. By dry distillation the resin yields a brown oil in which catechol can be detected. When fused with potash, it yields a quinone-like body. These results do not lead to any definite conclusion as to the origin of the resin, but they show that it is not identical with any of the resins in common use.

UROBILIN, syn. with HYDROBILIRUBIN (pp. 921, 1063). See further L. Disqué (*Zeitschr. physiol. Chem.* ii. 360; *Jahresb. f. Chem.* 1878, 1002).

UROCANINIC ACID. This name is given by Jaffe (*Ber.* viii. 811) to a substance having the composition $C^{12}H^{12}N^4O^4$, which he has obtained from dogs' urine. It reacts both as acid and as base, and melts at 212°–213°, giving off water and carbon dioxide, and leaving a strong base, $C^{11}H^{10}N^4O$, called urocauine. This base dissolves readily in alcohol, sparingly in water, and forms a red pulverulent platinum salt which melts in hot water.

UROCHLORALIC ACID, $C^7H^{12}Cl^2O^8$. This acid was found in the urine of persons who had for some time taken 5 or 6 grams. of chloral hydrate in the evening. It is extracted from the urine, after concentration and acidulation with sulphuric acid, by a mixture of alcohol and ether. It crystallises in colourless silky needles, dissolves in water, alcohol, and a mixture of alcohol and ether, but is insoluble in pure ether; forms well-crystallised salts with potassium, sodium, barium, and copper (v. Mering & Musculus, *Ber.* viii. 662).

UROFUSCO- and UROBUBRO-HEMATIN. Two peculiar colouring matters obtained by F. Baumstark (*Ber.* vii. 1170) from the urine of a patient suffering from Lepa. *Urobubrohematin*, $C^{26}H^{24}N^4Fe^2O^{28}$, is a blue-black light mass, insoluble in water, alcohol, ether, chloroform, and solution of common salt; soluble in the fixed alkalis and in ammonia, in alkaline phosphates and carbonates, and in acidulated alcohol; sparingly soluble in dilute sulphuric acid, and in solution of common salt acidulated with hydrochloric acid. The acid solution exhibits a characteristic absorption-spectrum. *Urofuscohematin*, $C^{26}H^{106}N^4O^{28}$, is black, pitchy, insoluble in water, alcohol, ether, chloroform, acids, and in solution of common salt, either neutral or mixed with hydrochloric acid; soluble in the fixed alkalis, ammonia, alkaline phosphates and carbonates, and acidulated alcohol.

URONITROTOLUENIC ACID, $C^{13}H^{15}NO^8$. An acid occurring, in combination with urea, in the urine of dogs to which orthonitrotoluene has been administered. See TOLUENES (NITRO-), (p. 1994).

UROKANIC ACID, $C^9H^8N^4O^8$. The potassium salt of this acid is formed when a solution of uric acid in potash-ley is left in contact with the air, but protected from access of carbonic acid. It decomposed when heated with ammonia at 60°, and the lead salt prepared from the viscid mass remaining in the retort has the composition of lead allantate (E. Mulder, *Ber.* viii. 1291).

USNIC ACID, $C^{18}H^{18}O^8$ (Paternò, *Ber.* ix. 345; *Gazz. chim. ital.* 1878, 225). This acid was discovered in 1840 by Knop in several lichens of the genera *Usnea*, *Parmelia*, *Evernia*, *Cladonia* and *Lecanora*; and nearly at the same time Reehleder & Heldt observed its presence in *Cladonia rangiferina* and *Usnea barbata* (Fries). Stenhouse, in 1846, found usnic acid in *Evernia prunastri*, and obtained, by dry distillation of the crude acid, a new substance which he named *betaorcin*. Hesse, in 1861 (*ibid.* cxvii. 343), observed that the acid extracted from *Cladonia rangiferina* melted at 175°, and therefore regarded it as isomeric with Knop's usnic acid, distinguishing it as *beta-usnic acid* (v. 970; vii. 353, 1194); and in 1866 the same chemist, in examining *Usnea barbata* (Hoffm.), extracted from it a new yellow crystalline substance, deceptively like usnic acid in most of its properties, but differing from it slightly in composition, and melting at 195°–4° (usnic acid at about 200°). This substance he designated as *carbusnic acid*, assigning to it the formula $C^{18}H^{16}O^8$, usnic acid being at that time generally regarded as $C^{18}H^{18}O^7$ (vi. 413).

The existence of beta-usnic acid was corroborated in 1870 by Stenhouse, who

Moreover showed (correcting a former statement) that beta-orcin was a derivative, not of usnic acid, but of the acid extracted from *Cladonia rangiferina*, for which he proposed the name *cladonic* instead of beta-usnic acid.

The existence of the second acid (carbusnic) was supposed to be confirmed by the difference of the results obtained by Paternò and by Salkowski with the acids prepared from *Zeora sordida* and from *Usnea barbata*, Fr. (*florida*, Hoffm.), notwithstanding that the supposition of Salkowski's acid being carbusnic acid was to a certain extent in contradiction to his own analyses of the salts of this acid, which gave for it an equivalent number (molecular weight) between 329.7 and 347.1, whereas the formula $C^{18}H^{16}O^8$ requires 372.

Finally, Hesse in his last memoir has re-examined the acid prepared from *Usnea barbata*, Hoffm., with results which he regards as confirmatory of those previously obtained. He is still of opinion that the lichen just mentioned contains an acid having the composition $C^{19}H^{16}O^8$, mixed perhaps with a small quantity of usnic acid. This conclusion is based on the result of two combustions of the acid, which gave, as a mean, 61.72 p. c. C and 4.42 H (the formula $C^{19}H^{16}O^8$ requiring 61.29 and 4.30), and on analyses of the potassium salt. This salt crystallises from alcohol of 93 p. c. in yellow flattened prisms containing 4.09 p. c. water and 9.46 potassium, and from dilute alcohol in beautiful pale-yellow leaflets containing 11.18 water and 8.97 potassium. These results agree tolerably well with the formulae $C^{18}H^{15}KO^8 + H^2O$ (4.20 H₂O and 9.15K), and $C^{18}H^{15}KO^8 + 3H^2O$ (11.63 H₂O and 8.47K), and are regarded by Hesse as affording decided confirmation of the existence of carbusnic acid, $C^{18}H^{16}O^8$.

On the other hand, Paternò finds that usnic acid from *Zeora sordida*, from which he has prepared decarbusnic $C^{18}H^{16}O^7$, pyrousnic acid $C^{17}H^{15}O^5$, and other well-defined compounds, yields, when boiled with potassium bicarbonate in such quantity as to leave a little of the acid undissolved, a potassium salt which crystallises from water in a mass of yellow leaflets giving off 12.23 p. c. water at 110°; from alcohol of 93 p. c. in yellow prisms containing 4.32 p. c. water and 9.48 p. c. potassium (or 9.91 calculated on the dry salt); and from alcohol of 51 p. c. in pale yellow leaflets containing 12.19 p. c. water and 8.64 potassium (9.84 for the dry salt).

These results agree very nearly with those which Hesse obtained with the potassium salt of the acid prepared from *Usnea barbata* (Hoffm.), but they are more in accordance with the formula $C^{18}H^{17}KO^8$ for the dry salt, than with $C^{18}H^{15}KO^7$, which would correspond with $C^{18}H^{16}O^7$, the formula originally assigned by Paternò to usnic acid.

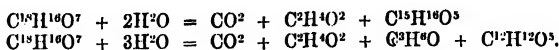
	$C^{18}H^{17}KO^8 + 3H^2O$			$C^{18}H^{17}KO^8 + H^2O$		
	Calc.	Exp.		Calc.	Exp.	
Water . . .	11.89	Paternò. Hesse.	12.19 11.49	4.30	Paternò. Hesse.	4.11
Potassium . .	8.59	8.64	8.97	9.33	9.48	— 9.46

Anhydrous salt, $C^{18}H^{17}KO^8$.

	Calc.	Paternò.
Potassium . . .	9.75	9.91 and 9.84

Knop also, in 1843, found in dried potassium usnate 9.16 p. c. potassium, which agrees better with $C^{18}H^{17}KO^8$ than with $C^{18}H^{15}KO^7$, the latter requiring 10.20 p. c. potassium.

On the other hand, the experiments of Paternò on the derivatives of the compound hitherto called usnic acid (extracted from *Usnea barbata* and *Zeora sordida*) have clearly shown that it has the composition $C^{18}H^{16}O^7$; and since this compound, when treated with alkalis, yields salts having the composition $C^{18}H^{16}M''O^7$, it must be inferred to be, not an acid, but an anhydride, a view which is confirmed by other facts and considerations. Thus the formation of carbusnic acid, $C^{18}H^{16}O^8$, and pyrousnic acid, $C^{17}H^{15}O^5$, from the compound $C^{18}H^{16}O^7$ (*infra*), may be represented by the equations—



Here the elimination of CO^2 from the compound $C^{18}H^{16}O^7$ is accompanied by assumption of the elements of water, which would not be necessary if this compound were really an acid containing the group CO^2 in the form of $CO.OH$, as in the transformation of benzoic, salicylic, and orsellinic acids into benzene, phenol, orcin, &c.

The experiments above detailed are sufficient to establish the identity of Hesse's carbusnic acid from *Usnea barbata*, Hoffm., with usnic acid. The carbusnic acid which Salkowski obtained from *Usnea florida*, Hoffm., is also identical therewith, inasmuch as Paternò has found that when boiled with aniline, it yields two compounds identical with those obtained from usnic acid, one melting at 142°, the other at 170°.

The acid regenerated from these compounds by hydrochloric acid is converted by heating with alcohol in a sealed tube into decarbusnein, $C^{15}H^{16}O^3$.

The so-called *usnetic acid*, $C^6H^{10}O^3$, recently found by Hesse in the mother-liquors of usnic acid from *Usnea barbata*, is regarded by Paternò as identical with decarbusnein.

Decarbusnein, $C^{15}H^{16}O^3$, obtained by heating usnic acid at 150° with three or four times its weight of alcohol, crystallises in yellow silky needles, which turn reddish in the air, melt at 175° , and decompose at a higher temperature. It dissolves in hot alcohol, sparingly also in water and in ether; does not colour ferric chloride, but when heated to 200° with alcohol and water, it yields an amorphous substance which colours ferric salts; acetyl chloride does not act upon it; nitric acid acts violently, forming oxalic acid. It reduces warm ammoniacal silver nitrate, with formation of an amorphous reddish-yellow substance.

Pyrousnic Acid, $C^{12}H^{12}O^3$, is prepared by gradually heating usnic acid to boiling with $2\frac{1}{2}$ pts. potash-solution in an atmosphere of hydrogen, and remains, on acidifying the brown solution with hydrochloric acid, then shaking it with ether, and leaving the ether to evaporate, in shining scales which melt with partial decomposition at 195° , and dissolve freely in alcohol and in boiling water. Its alkaline solutions rapidly absorb oxygen, turning green and ultimately brown. The ammoniacal solution quickly reduces silver nitrate.

UVIC ACID, CHO . Syn. with PYROTARTARIC ACID (p. 1724).

UVITIC ACID, $C^6H^4O^4 = C^6H^2(CO^2H)(CH^3)^2CO^2H$. *Symmetrical Methylisophthalic acid*. Mesidic acid (v. 970; vi. 821). This acid, intermediate in composition between mesitylenic acid, $C^6H^3(CH^3)^2CO^2H$, and trimelic acid, $C^6H^2(CO^2H)^3$, is formed: α . By oxidation of mesitylenic acid (vi. 821); β . Together with uvitonic acid and other products, by heating pyracemic acid with excess of barium hydrate, or by the action of heat on normal barium pyracemate (p. 1717); probably also, together with oxalic acid and urea, by boiling pyruil with baryta-water (p. 1718). β . By oxidation of methyl-diethyl-benzene and of ethyl-dimethyl-benzene (p. 1285).

Nitro- and Amido-uvitic Acids (Böttiger, *Ber.* ix. 804). Uvitic acid heated for several days with a mixture of strong sulphuric and fuming nitric acids, yields two mononitro-derivatives, separable by their different degrees of solubility in water, together with dinitro-derivatives and several products of oxidation.

α -*Mononitrouvitic acid*, $C^6H^2(NO^2)O^4 + 2H^2O$, the chief product of the reaction, dissolves but very sparingly in cold water, a little more freely in boiling water, and crystallises in groups of needles or long prisms, melting at 226° – 227° , and containing 2 mols. water. Its potassium-salt is very soluble and forms microscopic needles containing 1 mol. of water. The barium salt dissolves but sparingly in hot water, and forms slender needles which lose 1 mol. water at 150° . The calcium-salt, which is more soluble, crystallises in needles with 3 mols. of water.

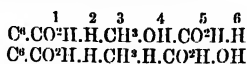
β -*Mononitrouvitic acid* is much more freely soluble in water than the α -acid, and forms acute rhombohedrons, melting at 249° – 250° , and containing half a molecule of water. The two nitro-acids treated with tin and hydrochloric acid, yield the corresponding amido-acids.

α -*Amidouvitic acid* is insoluble in water and sparingly soluble in hot alcohol, from which it crystallises in small yellow needles, melting and decomposing at 240° . Its impure alcoholic solution shows a splendid greenish-blue fluorescence, but that of the pure acid is less beautiful and of a reddish-blue. When this acid is stirred up with water to a thick paste, and nitrous gas is passed into the mixture, it liquefies, and on addition of alcohol and ether, deposits the corresponding diazo-compound as a hygroscopic mass which quickly turns red on exposure to the air, and when heated with water yields a hydroxyuvitic acid (*infra*).

β -*Amidouvitic acid* forms a yellow crystalline powder or light-yellow needles; it is nearly insoluble in water, and melts, with decomposition, at 250° – 255° . The alcoholic solution of the impure acid exhibits a greenish-blue, the alcoholic-aqueous solution of the pure acid a fine reddish-blue fluorescence. The tin-salt of this acid is very sparingly soluble and is not decomposed by water. The β -amido-acid yields a moderately stable diazo-compound, which when heated with water is converted into β -hydroxyuvitic acid.

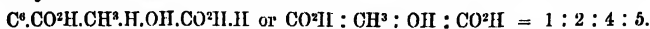
Hydroxyuvitic Acids, $C^6H^2(OH)(CH^3)(CO^2H)^2$. Two of these acids, α and β , are obtained, as already observed, by the action of boiling water on the corresponding

azo-acids. As uritic acid has the symmetrical constitution 1 : 3 : 5, these two hydroxy-acids must be represented by the formulæ :



but it has not yet been ascertained which of these formulæ must be assigned to the α -acid (m.p. 285°), and which to the β acid (m.p. 220°).

Another hydroxyuritic acid (or more properly *hydroxyxylicidic acid*) is formed (as ethylic ether) by the action of chloroform on a mixture of ethylic acetosodacetate and sodium ethylate, or on the crude product of the action of sodium on acetic ether, which contains both these bodies. Its constitution, as already shown (p. 17), is represented by the formula :



By dry distillation of its calcium or barium salt it is converted into *meta*-cresol (Oppenheim a. Pfaff, pp. 17 and 1477).

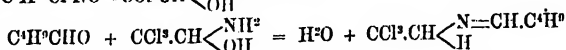
UVITONIC ACID, $\text{C}^6\text{H}^{12}\text{O}^7$ (?). This acid is one of the products obtained by boiling pyroracemic acid with excess of barium hydrate, and probably also by the action of heat on barium pyroracemate (p. 1717). It is partly converted into uritic acid when left in contact with the air, and completely by prolonged treatment with barium hydrate (Böttinger, *Ber.* ix. 836).

UVITONINIC ACID, $\text{C}^6\text{H}^8\text{NO}^4$. The acid ammonium salt of this acid is obtained as a precipitate, together with carbonic and acetic acids, by the action of alcoholic ammonia on pyroracemic acid. Its barium salt contains $\text{C}^6\text{H}^8\text{NO}^4\text{Ba} + 3\text{H}^2\text{O}$; the *siletr* salt, $\text{C}^6\text{HNO}^4\text{Ag}^2 + \text{H}^2\text{O}$. The acid is not acted on by nitric acid. Chromic acid oxidises it to carbon dioxide, ammonia and acetic acid (Böttinger, *Ber.* x. 362).

VALERAL or VALERALDEHYDE, $\text{C}^5\text{H}^8\text{O} = \text{C}^5\text{H}^7\text{CHO}$. This compound is formed, together with methylisopropyl ketone, by the action of zinc chloride or phosphorus pentoxide on isopropylethylglycol (Flawitzky, *Ber.* x. 2240).

Valeral and *acetyl chloride* heated together at 100° in a sealed tube unite and form the compound $\text{C}^5\text{H}^{10}\text{O.C}^2\text{H}^3\text{OCl}$, which is a liquid having a density of 0.987 at -17°, boiling at 118-128°, and gradually decomposed by water into acetic acid, hydrochloric acid, and valeral (Maxwell Simpson, *Proc. Roy. Soc.*, xxvii. 120).

Valeral and *chloral ammonia* unite, with elimination of H^2O , forming the compound $\text{C}^5\text{H}^7\text{Cl}^2\text{NO} = \text{CCl}^2\text{CH} \begin{smallmatrix} \text{N} \\ \text{OH} \end{smallmatrix} \text{CH.C}^4\text{H}^9$



(R. Schiff, *Ber.* xi. 1694).

Valeral and *benzidine* unite in the proportion of 2 mol. $\text{C}^5\text{H}^{10}\text{O}$ to 1 mol. $\text{C}^{12}\text{H}^{12}\text{N}^2$, forming a sparingly soluble compound (H. Schiff, *Ber.* xi. 830).

Polymerides. The polymeric valeral $n\text{C}^5\text{H}^{10}\text{O}$, homologous with aldol, which Borodin obtained by the action of sodium, or of potassium hydroxide at 0°, on valeral (vii. 1196) has been further examined by the same chemist (*Ber.* vi. 982), also by Gass a. Hell (*ibid.* viii. 369), and by Bruylant's (*ibid.* 414). It is a colourless viscid liquid, which, when heated, is converted, with elimination of water, into a condensation-product, viz. an aldehyde $\text{C}^{10}\text{H}^{18}\text{O}$, and a neutral body $\text{C}^{20}\text{H}^{36}\text{O}^2$, together with valeral, the decomposition being exactly analogous to that of aldol under similar circumstances. The polymeric valeral further resembles aldol in depositing crystals when left for some time in contact with dilute soda-ley. This, however, does not always take place, and the amount formed and the rate of formation vary greatly in different experiments conducted apparently under precisely similar conditions; in fact, the conditions under which these crystals are produced have not yet been ascertained. The composition of the air-dry crystals is represented by the formula $(\text{C}^{10}\text{H}^{20}\text{O}^2)^2\text{H}^2\text{O}$. When heated, they melt slowly to a colourless liquid, which, if not heated too long, solidifies to a crystalline mass on cooling. If it be heated above the melting point, decomposition takes place, valeral passing over first, then the aldehyde $\text{C}^{10}\text{H}^{18}\text{O}$, and finally the compound $\text{C}^{20}\text{H}^{36}\text{O}^2$; these products are obtained quite colourless, and no residue

remains in the retort. The crystals are similarly decomposed when heated with water or very dilute sulphuric acid; they are also decomposed, with loss of water, when exposed over sulphuric acid.

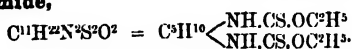
Güss a. Hell obtain a polymeric valeral by prolonged contact of valeral with recently ignited potassium carbonate, the valeral thickening, and acquiring in a few days at ordinary temperatures, more quickly at 50° – 60° , the consistence of honey. This polymeride is permanent in sunshine, and does not unite either with ammonia or with alkaline bisulphites; by distillation or by heating in a sealed tube it is reconverted into ordinary valeral. Its consistence varies with the temperature; at 60° – 70° it is comparatively mobile, but at -45° it is so viscid as to be no longer capable of running; it does not however solidify completely. Bruylants, on the other hand, by pressing the thickened mass between paper, after washing it with water, obtained a solid body, which, after recrystallisation from ether, formed slender silky needles, having the percentage composition of valeral, and yielding a vapour having the density of that substance, showing that the polymeride undergoes dissociation when heated. The crystals are insoluble in water, but dissolve readily in alcohol, still more readily in chloroform and carbon bisulphide. They melt at 83° – 84° , and decompose at a higher temperature, yielding a liquid which unites like an aldehyde with bisulphites and silver-solution, and does not easily resolidify on cooling.

Condensation-products of Valeral (Güss a. Hell, *Ber.* viii. 369). These are obtained by boiling valeral with solution of potassium carbonate. The liquid, which at first is turbid, becomes clear after about two hours' boiling, the reaction being then complete. The change affects, however, only about half the quantity of valeral present, which is thereby converted into products of higher boiling point, the other and somewhat larger portion remaining unaltered. The residue left after distilling off this unaltered valeral is resolved by fractionation into three portions, the largest, which boils at 187° – 191° (189.9° – 194° corr.) under a pressure of 742 mm., having the composition $C^{10}H^{18}O = 2C^5H^{10}O - H^2O$; the second, which is much smaller in quantity and boils at 235° – 240° , being represented by the somewhat doubtful formula $C^{18}H^{28}O^2 = 3C^5H^{10}O - H^2O$; while a third, which boils apparently at 265° – 270° , has the composition $C^{10}H^{30}O^3 = 4C^5H^{10}O - H^2O$, and is resolved by prolonged distillation into water, the compounds above mentioned, and others of higher boiling point.

A condensation-product having the formula $C^{20}H^{34}O^3$ was obtained by Borodin, who, however, describes it as boiling without decomposition (vii. 1196). The body $C^{10}H^{18}O$ was previously obtained by Riban and by Kekulé (*loc. cit.*) Güss a. Hell describe it as a yellowish oil, which gradually becomes colourless on exposure to light and assumes a viscid consistence at low temperatures, but does not solidify completely even at -45° . Sp. gr. = 0.861 at 0° , 0.851 at 14° , referred to water at 0° . The compound has a strong odour like that of amyl valerate, and is insoluble in water, but dissolves readily in alcohol and ether. It does not unite with ammonia, nor (contrary to Borodin's statement) with bisulphites; but it reduces silver oxide on boiling, also an ammoniacal solution of silver. It acts violently on phosphoric anhydride, forming hydrocarbons of the formula nC^5H^8 ; with bromine it yields an oily product. It is not attacked by water even at 250° . By boiling with alcoholic potash it is converted partly into valeric acid, but for the greater part into a brown viscid condensation-product, apparently $C^{30}H^{52}O^2$, which cannot be distilled either alone or with vapour of water.

Valeral-ammonia, $C^5H^{10}O.NH^3 = C^5H^9.CH(NH^2)OH$ (Ijubavin, *Ber.* vi. 1460). This compound is formed immediately by the action of ammonia on pure valeral. slowly, on the other hand, when impure valeral is used. In the fused state it may be dehydrated by solid caustic alkalis without decomposition. It is decomposed by alcohol of 95 per cent. The dry compound, when distilled, first gives off a large quantity of ammonia, then at 250° a mixture of valeral-ammonia and Erdmann's trioxamylidene or trioxamylamine, $(C^5H^{10}O)^3.NH^3$ (v. 886); the same products, together with valeral, are formed on distilling valeral-ammonia with aqueous vapour at 100° , also on boiling valeral-ammonia with potash. The alcoholic solution of valeral-ammonia, when left to itself for some time, likewise yields trioxamylamine. This base, treated with hydrochloric acid, forms white flocks, melting at 112° – 113° and consisting of a mixture of $C^5H^9.NO^2.HCl$ and $C^5H^{11}.NO^2.HCl$.

Valeral-xanthamide,



On adding hydrochloric acid to a mixture of xanthamide and valeral a glutinous mass is formed, which on addition of a small quantity of alcohol breaks up without dissolving, and yields with water a yellowish white or pure white crystalline powder made up of small indistinct cohering laminae. This is the compound above formu-

lated. It has a faint, peculiar odour, dissolves but sparingly in ether, more readily in alcohol, and melts at 108° . When heated in the dry state it emits an odour of mercaptan, and at the same time gives off ammonia and cyanic acid, and finally strongly alkaline vapours having an intensely repulsive odour (C. Bishoff, *Ber.* vii. 1078).

VALERIC ACID. $C^5H^{10}O^2 = (CH^3)^2CH.CH^2.COOH$. *Isopentoic, Isopropyl-acetic, Isobutylformic Acid.*—See PENTOIC ACIDS (p. 1500). The properties of this acid and of several of its salts and derivatives have lately been fully investigated by E. Schmidt and R. Sachtlohen (*Liebigs Annalen*, xciii. 87). The acid was prepared by a slight modification of Erlenmeyer and Hell's process, in which isobutyl cyanide is decomposed by alcoholic potash (vii. 1197). The free acid boils at 175° under a pressure of 754.8 mm. Sp. gr. 0.93087 at 17.4° . It is optically inactive.* Its salts are partially converted into basic compounds on keeping; their aqueous solutions have a slightly acid reaction. The alkaline and alkaline-earth salts are easily soluble in water, but those of the heavy metals are difficultly soluble, and generally more soluble in cold than in hot water. The calcium salt, $(C^5H^9O^2)^2Ca + 3H^2O$, is more soluble than that of active valeric acid, and is not so prone to form basic salts. The manganese salt, $(C^5H^9O^2)^2Mn + 2H^2O$, the zinc salt, $(C^5H^9O^2)^2Zn + 2H^2O$, and the copper salt, $(C^5H^9O^2)^2Cu$, are more soluble in cold than in hot water. Quinine isobutylformate, $C^{20}H^{24}N^2O^2.C^5H^{10}O^2$, closely resembles the active valerate. Methyl isobutylformate, $C^9H^{18}O^2.CH^3$, is a colourless liquid with a pleasant fruity odour (b. p. 117° at 763.8 mm.) Sp. gr. at $17^{\circ} = 0.885465$.

Isobutylformamide, $C^5H^9O.NH^2$, is prepared by heating the methylic ether with a mixture of aqueous and alcoholic ammonia for five hours at 120° in sealed tubes, and evaporating the product over sulphuric acid. It crystallises in silky plates (m. p. 135°), which are easily soluble in water and alcohol, and can be sublimed.

Isobutylformanilide, $C^5H^9O.NH(C^6H^5)$, is obtained by boiling the acid and aniline together in molecular proportions for two days. It is sparingly soluble in hot water, but dissolves easily in alcohol or ether. It sublimes when heated, and volatilises in a current of steam (m. p. 100°).

Bromisobutylformic acid seems to be formed when isobutylformic acid is heated with bromine at 140° , but it has not been obtained pure.

Amido-isobutylformic acid (Isopropylglycocine), $NH^2.C^5H^8.COOH$, is prepared by heating bromisobutylformic acid with 4 vols. of concentrated ammonia in sealed tubes for six hours at 130° , removing the ammonia by evaporation, digesting the residue with lead hydroxide until it ceases to smell of ammonia, collecting the precipitated lead bromide on a filter, and removing the lead in solution by sulphuretted hydrogen; the filtrate, on evaporation over sulphuric acid, solidifies to a yellow crystalline mass, which may be purified by washing with a mixture of alcohol and ether and crystallisation from alcohol.

Amido-isobutylformic acid crystallises in colourless plates, which are easily soluble in water, but difficultly soluble in alcohol and ether. When heated, it volatilises without melting. In these properties it agrees entirely with Clark and Fittig's amido-valeric acid (v. 278).

Hydroxyisobutylformic acid, $C^5H^8(OH).COOH$, is obtained by boiling bromisobutylformic acid with a slight excess of concentrated potash for a short time. After separating the potassium bromide and acidifying with strong hydrochloric acid, a yellow oil separates, which consists essentially of isobutylformic acid; this is removed, and the hydroxyisobutylformic acid extracted from the acid liquid by agitation with ether; on distilling off the latter, a yellow syrup remains, from which colourless crystals separate after some time. The acid may be purified by crystallisation from ether. Hydroxyisobutylformic acid (m. p. 82°) and its salts do not differ in any of their properties from those of the hydroxy-acid and salts obtained by Clark and Fittig (vi. 894) from ordinary valeric acid.

Ethylic hydroxyisobutylformate, $C^5H^9O^2.C^2H^5$, is obtained by the action of ethyl iodide on the silver salt. It is a colourless liquid of pleasant odour, and is lighter than water, in which it is but slightly soluble. It boils at 175° with slight decomposition. Treated with phosphorus trichloride, it does not give an acid identical or isomeric with angelic acid, but amorphous phosphides and a highly chlorinated oil.

Valerolactide, $C^5H^8O^2$, is obtained when hydroxyisobutylformic acid is heated in sealed tubes at 200° for six hours, thus:— $C^5H^{11}O^3 = C^5H^8O^2 + H^2O$. It crystallises in white needles melting at 126° , boiling at 220° – 240° , insoluble in cold water, and melting in hot water to a colourless oil. It is easily soluble in alcohol and ether, and may be sublimed in silky needles. It is not attacked by dilute alkaline solutions.

* Active valeric or pentoic acid is methylethylacetic acid, $(OH^3)(C^2H^5)OH.COOH$ (p. 1501).

Trichlor-hydroxyvaleric or *Trichlorovalerolactic acid*, $C^3H^3Cl^3O^3$, formerly described by Pinner and Bischoff, forms the following salts:—The *sodium salt*, $C^3H^3NaCl^3O^3 + H^2O$, loses its water of crystallisation at 100° . The *ammonium salt* forms small granular crystals, and the *lead salt* is an amorphous precipitate. The *acetyl-compound*, $C^5H^4(C^2H^3O)Cl^3O^3 + H^2O$, which crystallises in white needles (m. p. 84°), is prepared by digesting the acid with acetic anhydride and pouring the product into cold water. It is insoluble in cold water, and is slowly decomposed by boiling with water. The anhydrous compound forms a thick uncrystallisable syrup.

Ethyllic trichlorhydroxyvalerate, $C^5H^4Cl^3O^3.C^2H^3$, forms long prismatic crystals, which melt at 40° and boil at 255° . If this ester is dissolved in alcoholic ammonia, and the solution left at rest for several weeks, a white crystalline crust is formed, which consists of a mixture of ammonium chloride and the amide of *monochlorimidoangelic acid*, $C^5H^4ClN^2O$. This amide is soluble in hot benzene, and is reprecipitated by the addition of light petroleum to this solution; melts with decomposition at 118° . Platinum chloride and silver nitrate produce precipitates in the aqueous solution (Pinner & Klein, *Ber.* xi. 1488).

VALERITRINE, C^5H^7N . This base, obtained by heating 1 volume valeral with 2 volumes alcoholic ammonia at 150° (vii. 1200), has been further examined by Ljubavin (*Ber.* vi. 566). To purify it, the hydrochloride, which forms an uncrystallisable syrup, is mixed with caustic potash, and the base thereby set free is distilled off with steam, precipitated from alcoholic solution by picric acid, and again set free by an alkali.

Valeritrine is a colourless, very mobile liquid, having great dispersive power, boiling at 250° – 260° , easily soluble in alcohol, ether, and weak acids, nearly insoluble in water and aqueous alkalis. Its salts are mostly uncrystallisable, dissolve easily in water, and are decomposed by boiling therewith. The base is on the whole very stable, and is not decomposed by sodium even at 250° . The *platinochloride*, $(C^5H^7N.HCl)^2PtCl^4$, crystallises in transparent, brittle, orange-coloured granules, easily soluble in alcohol, sparingly in water and in ether; in boiling water it melts to an oil, which floats on the surface and gradually dissolves. The *mercurochloride*, $C^5H^7N.HCl.HgCl^2$, forms rhombohedral crystals, which dissolve in boiling dilute alcohol and melt at 86° – 88° . The *picrate*, $C^5H^7N.C^6H^3(NO^2)^3O$, purified by crystallisation from warm alcohol, forms needles melting at 129° – 130° , sparingly soluble in cold, freely in warm alcohol.

VALEROLACTIDE, $C^5H^6O^3$. On the modification of this compound, formed by the action of heat on hydroxyisobutylformic acid, see p. 2085.

VALERYLENES, or **PENTINES**, C^5H^8 (see p. 1500). According to Boucharlat (*Compt. rend.* lxxxvii. 654), valerylene (which modification?), heated for about six hours at 250° – 260° in a sealed tube filled with carbon dioxide, is converted into a terpilene, C^5H^{16} , which, after several rectifications, has a density of 0.848 at 0° , and 0.836 at 15° , and distils at about 180° . The condensation of the same valerylene also gives rise to a trivalerylene, $C^{15}H^{21}$, which is found in the portion of the crude product distilling between 240° and 250° , and yields a monohydrochloride, which is completely decomposed by heat.

Methyl-ethylacetylene, $C^2H^3.C\equiv C.CH^3$, is obtained by the action of alkalis on methylethyl-ethylene bromide, $C^2H^3.CHBr.CHBr.CH^3$, and forms the portion of commercial valerylene which is insoluble in sulphuric acid. It boils at 51° (Eltzoff, *Bull. Soc. Chim.* [2] xxix. 210), and is converted by oxidation with chromic acid mixture into propionic and acetic acids.

Isopropylacetylene, $(CH^3)^2CH.C\equiv CH$. Flawitzky & Kriloff (*Ber.* x. 110; *Bull. Soc. Chim.* [2] xxix. 214) have prepared this modification of valerylene from the mixture of pentylenes obtained from amyl iodide, by heating the bromides of these pentylenes with alcoholic potash on a water-bath in a flask with reversed condenser. According to their observations it boils at 28° – 30° , not at 35° , as found by Bruylants and Eltzoff (p. 1500). By oxidation with potassium dichromate and sulphuric acid it yields acetone and lactic acid, and when treated with sulphuric acid it yields methylisopropyl ketone, $(CH^3)^2CH.CO.CH^3$, together with products of higher boiling point.

VALERYL-TRIMETHYLAMMONIUM CHLORIDE, $(C^5H^8)(CH^3)^3NCl$, is prepared by digesting trimethylamine with commercial amylenic chloride for several days at 50° – 60° . It is very hygroscopic, and forms a *platinum salt*, $(C^5H^8NCl)^2PtCl^4 + H^2O$, which crystallises in hemispherical groups of irregular laminae. The *gold salt*, which is anhydrous, melts when heated, without loss of weight, and solidifies in the crystalline state on cooling (Harnack, *Chem. Centr.* 1876, 560).

VANADIUM. Atomic weight 51. Lockyer has detected this element in the sun by the coincidence of nine lines in the solar spectrum and in that of incandescent

vanadium (*Proc. Roy. Soc.*, xxvii. 279). The presence of vanadium in a meteorite from Adare, County Limerick, has been demonstrated by R. Apjohn (*Chem. Soc. J.* xxvii. 104).

J. Walz (*Amer. Chemist*, vi. 453) has demonstrated the widely diffused occurrence of vanadium, especially in primary iron ores, having found it in all the American magnetic iron ores which he examined. He has also observed an intimate connection between the occurrence of vanadic and titanitic acid, all the ores which contain the latter in relatively large quantity being also proportionately rich in the former.

On the preparation of Vanadium from the uranium ore of Joachimsthal, see Paterna (*Dingl. pol. J.* cxxxxi. 556).

On the physiological action of Vanadium, see J. Priestley (*Proc. Roy. Soc.* xxiv. 40; *Jahresb. f. Chem.* 1877, 887).

On the industrial uses of Vanadium compounds, see J. Philipp (*Hofmann's Entwicklung der Chemischen Industrie*, p. 836) and R. v. Wagner (*Dingl. pol. J.* cxxxiii. 631).

Estimation.—To estimate small quantities of vanadium in *silicates*, V. Roussel (*Compt. rend.* lxxvii. 1102) fuses the substance with sodium carbonate; oxidises it with a small quantity of nitre; exhausts the cooled and pulverised melt with boiling water; washes it completely; evaporates; precipitates with ammonium carbonate; filters; adds ammonium sulphide; leaves the liquid at rest for several days; again filters; adds hydrochloric acid, which throws down vanadium sulphide mixed with sulphur; and weighs the precipitate after expelling the free sulphur by ignition.

For the volumetric analysis of *vanadium sulphates* and double sulphates with alkali-metals, Gerland (*Ber.* x. 1216) reduces the vanadic acid by means of sulphurous acid to vanadium tetroxide, which is stable in acid solution, but is completely oxidised to vanadic acid by permanganate. On the other hand, vanadium tetroxide may be advantageously used for the titration of permanganate solutions.

To separate vanadium from *thallium*, Carnelley (*Chem. Soc. J.* xxvi. 323) mixes the solution of the two metals in sulphuric acid with a small quantity of sulphurous acid; precipitates the thallium with potassium iodide; evaporates the filtrate; fuses the residue with sodium carbonate; and saturates the aqueous solution of the melt with sal-ammoniac. The ammonium metavanadate which separates after twelve hours is washed, first with a saturated solution of sal-ammoniac, then with alcohol, and converted by ignition into vanadium pentoxide.

Vanadic acid may be separated from *alumina* by dissolving the compound (ardennite, for example) in a small quantity of hydrochloric acid, and digesting the solution for a short time on the water-bath with a few drops of phosphoric acid, whereby the aluminium vanadate is completely converted into aluminium phosphate, which may be completely precipitated by ammonia, while the whole of the vanadium remains in solution (Bettendorff, *Ann. Phys. Chem.* clx. 126).

Compounds of Vanadium.

Ethylchloride, $V(OC^2H^5)^2Cl^2$. This compound is formed by the action of ethyl oxide on vanadium oxychloride. Equal parts of ether and the oxychloride are digested for two or three hours in a closed vessel at 60° – 70° , and the lighter of the liquids thereby formed is distilled under a pressure of 160–200 mm., whereby the ethylchloride is obtained in shining needle-shaped crystals melting at a temperature below 20° . It is slowly decomposed by water into ethyl oxide, vanadium pentoxide, and hydrochloric acid, and changes spontaneously into a brown liquid even in a sealed tube (P. P. Bedson, *Chem. Soc. J.* xxix. 309).

Ferrocyanides. See CYANIDES (p. 618).

Fluoride. According to A. Guyard (*Bull. Soc. Chim.* [2] xxv. 350) an anhydrous vanadium fluoride is given off in yellow vapours, when the oxyfluoride obtained by treating vanadic acid with hydrofluoric acid and a little alcohol is heated to redness.

Oxyhaloid Compounds. The tetroxychloride or vanadic oxychloride, $V^2O^4Cl^2 + 5H^2O$, is obtained by dissolving vanadic acid in strong hydrochloric acid, and reducing the solution with hydrogen sulphide. On evaporating to dryness on the water-bath, the oxychloride remains as a brown amorphous substance which forms a blue solution with water and a brown solution with alcohol and strong hydrochloric acid (J. K. Crow, *Chem. Soc. J.* xxx. 453). The same compound is described by A. Guyard (*Bull. Soc. Chim.* [2], xxv. 350; *Chem. Soc. J.* xxx. 173), who, however, calls it *chlorure vanadique*.

The corresponding oxybromide (*bromure vanadique*), easily obtained by treating vanadic acid with bromine-water and alcohol, or with hydrobromic acid, resembles the oxychloride, but decomposes more readily, with formation of vanadium tetroxide.

To obtain it in the dry state the solution must be evaporated at a temperature below 80° (Guyard, *loc. cit.*)

The oxyiodide, obtained by the action of hydriodic acid on the tetroxide, resembles the preceding compounds, and forms in the dry state a blackish-green, uncrystallisable mass.

The oxyfluoride, obtained by treating vanadic acid with hydrofluoric acid and a little alcohol, is less easily decomposable than the preceding compounds. At a red heat it is at first resolved into hydrogen fluoride and vanadium tetroxide, but afterwards gives off thick yellow vapours of anhydrous vanadium fluoride (Guyard).

A *silicofluoride* of vanadium is obtained by treating vanadic acid with silicofluoric acid and a small quantity of alcohol. The solution, which is blue at first, becomes green when concentrated, and ultimately yields a greyish uncrystallisable mass (Guyard).

Oxides and Oxy-salts of Vanadium. TETROXIDE or HYPOVANADIC OXIDE, V_2O_4 . This oxide, obtained either by slow oxidation of the trioxide in contact with the air, or by heating the tetroxychloride, $V_2O_4Cl_2$, in a stream of carbon dioxide, is a dark green, amorphous powder, insoluble in water, easily soluble in alkalis and in acids. When exposed to the air it gradually absorbs oxygen and is converted into the pentoxide.

The *hydrate*, $V_2O_4 \cdot 7H_2O$, prepared by careful precipitation of the sulphate or chloride, and filtered and dried out of contact with the air, forms a black amorphous mass having a vitreous fracture. It unites with bases, forming salts called Hypovanadates, and with acids, forming the Vanadyl Salts.

Hypovanadates. The *potassium salt*, $(V_2O_4)^2K_2O + 7H_2O$, forms dark brown, shining crystals, easily soluble in water, nearly insoluble in potash-ley, quite insoluble in alcohol. The *sodium salt*, $(V_2O_4)^2Na_2O + 7H_2O$, exhibits precisely similar characters. The *ammonium salt*, $(V_2O_4)^2(NH_4)_2O + 3H_2O$, is a brown crystalline mass. The *barium salt*, $(V_2O_4)^2BaO$, is obtained as a yellow-brown precipitate on adding barium chloride to a solution of $V_2O_4Cl_2$. The *lead salt*, $V_2O_4 \cdot PbO$, is a brown precipitate; the *silver salt*, $V_2O_4 \cdot Ag_2O$, a black crystalline powder (J. K. Crow, *Chem. Soc. J.* xxx. 453).

Vanadyl Salts (Crow, *loc. cit.*; Gerland, *Ber.* ix. 869, x. 2109). *Trisulphate*, $V_2O_4 \cdot 3SO_3$.—This salt forms two hydrates, one soluble, the other insoluble. (a) The *insoluble hydrate*, $V_2O_4 \cdot 3SO_3 + 4H_2O$, is prepared by treating a solution of the pentoxide in sulphuric acid with reducing agents, such as sulphurous acid, oxalic acid, hydrochloric acid, or alcohol, and evaporating, whereby a blue syrup is obtained, which on further heating, or better on addition of strong sulphuric acid, deposits the sparingly soluble hydrate in light blue, very slender needles, which may be purified by pouring off the mother-liquor, mixing them with water, avoiding all rise of temperature, and washing them on a filter with cold water, or better with dilute alcohol. These crystals dissolve but very slowly in cold water, and even more slowly in dilute alcohol, but are quickly dissolved by hot water. On exposure to the air they deliquesce to a blue mass having the consistence of honey. (b) *More soluble hydrate*, $V_2O_4 \cdot 3SO_3 + 15H_2O$. This hydrate is obtained by treating the concentrated solution of the above-described crystals with strong alcohol and repeatedly kneading the precipitate with fresh quantities of alcohol; it then forms a transparent waxy mass, which is not altered even by prolonged sojourn over strong sulphuric acid. The aqueous solution of either of these hydrates mixed with ammonium vanadate assumes a dark green colour, and remains clear at ordinary temperatures, but on boiling deposits a black precipitate, which adheres closely to the sides of the vessel, forming a hard specular crust, the solution at the same time becoming lighter in colour. Sodium phosphate produces in the same solution a greenish-blue precipitate, easily soluble in excess of the reagent and in acetic acid. Normal potassium chromate forms a yellow-brown precipitate. Vanadyl trisulphate unites with potassium sulphate, forming an easily soluble double salt, $V_2O_4 \cdot 3SO_3 + K_2SO_4$, which dries up over sulphuric acid to a clear syrup, and separates after some time in the form of a light blue powder (Gerland). A *hexhydrate*, $V_2O_4 \cdot 3SO_3 + 6H_2O$, is formed on evaporating the blue solution obtained by reduction of vanadium pentoxide dissolved in strong sulphuric acid (Crow).

Bisulphate, $V_2O_4 \cdot 2SO_3$.—This salt is known in two modifications—one soluble, the other insoluble, in cold water. The insoluble modification is formed on heating a solution of vanadium tetroxide in excess of sulphuric acid for several hours to the boiling point of sulphuric acid, and separates as a heavy microcrystalline powder, having a light grey-green colour. It is quite insoluble in cold water, and acquires a faint blue colour on prolonged boiling with water, more quickly in presence of hydrochloric or sulphuric acid. By prolonged heating at 400° it acquires a pure greenish-

blue colour, and is converted, without change of composition, into the soluble modification. In this state the salt dissolves completely when heated with water in sealed tubes at 130° , forming a deep blue solution, which, when evaporated over sulphuric acid, leaves a hard, resinous, transparent mass; and this, when moistened with dilute alcohol, changes in the course of a few weeks into a conglomerate of fine blue radiate crystals, having the composition $V^2O^4, 2SO^3 + 7H^2O$, and identical with the salt which Crow obtained by the action of alcohol on the trisulphate (*Chem. Soc. J.* xxx. 453). The crystals, when exposed to moist air, swell up considerably, absorbing 6 mol. H^2O more, and even deliquesce in a very damp atmosphere, but effloresce and turn white in dry air. A decahydrate, $V^2O^4, 2SO^3 + 10H^2O$, separates in groups of deep blue crystals an inch long from the solution of the preceding hydrate, when left to itself for a month; it is also formed on moistening the amorphous sulphate with water. Of the 10 mol. water of crystallisation five are given off very quickly at 100° , two more slowly, while the last three cannot be driven off even at 130° (Gerland, *Ber.* x. 2109).

Acid Vanadyl Sulphates.—Crow (*Chem. Soc. J.* xxx. 455), by dissolving vanadic oxide in strong sulphuric acid, and reducing the solution with sulphurous acid, obtained an acid vanadyl sulphate as a light blue crystalline powder, having the composition $V^2O^4, 3SO^3 + 6H^2O$ or $V^2O^4, 2SO^3, H^2SO^4 + 5H^2O$. Gerland (*loc. cit.*) has prepared two more of these salts. A solution of vanadium tetroxide in excess of sulphuric acid deposits an abundance of small blue transparent crystals, grouped in crusts; they are very deliquescent, and in contact with water, alcohol, or ether are thrown into rapid movement, and either dissolve or are converted into small silvery scales, which, when strongly magnified, appear as square plates or groups of cubes. The composition of the crusts appears to be represented by the formula $V^2O^4, 2SO^3, H^2SO^4 + 3H^2O$; that of the scales by $V^2O^4, 2SO^3, H^2SO^4 + 2H^2O$. This last compound is formed in larger quantity when a solution of the tetroxide in a large excess of sulphuric acid is heated at 140° – 160° , and it may be safely assumed to exist ready-formed in the crusts above-mentioned. This acid vanadyl sulphate, like many other vanadium compounds, possesses in a high degree the property of carrying down other soluble salts with it (Gerland).

Vanadic Sulphates, or Sulphates of Vanadium Pentoxide (Gerland, *Ber.* xi. 98; *Chem. News*, xxxvii. 127, 138). The pentoxide dissolves in sulphuric acid more or less readily, according to the manner in which it has been prepared, the fused oxide dissolving more slowly than that prepared by the ignition of ammonium vanadate. The trisulphate, $V^2O^5, 3SO^3$, is prepared by dissolving vanadic oxide in excess of sulphuric acid at a low temperature, the excess of sulphuric acid being afterwards removed by heating in an air-bath at 200° . The dry residue thus obtained is covered on the surface with a green compound, $V^2O^5, 2SO^3$, which is insoluble in water; and under this is the red crystalline compound, $V^2O^5, 3SO^3$. This latter salt absorbs water from the air, forming a red syrup, which, on addition of water, is decomposed, vanadic acid separating out. The separation of the two above-named sulphates is effected by heating the mixture with dilute nitric acid, $V^2O^5, 2SO^3$ remaining undissolved.

$V^2O^5, 3SO^3$ is also formed by boiling the pentoxide in sulphuric acid, and separates in ruby-red transparent octohedrons; but if the boiling be continued for some time, it crystallises in golden-yellow needles. The simultaneous formation of $V^2O^5, 2SO^3$, and the rapidity with which the trisulphate absorbs moisture, render its preparation and analysis difficult.

Solutions of V^2O^5 in excess of sulphuric acid, heated for some time at 130° – 150° , yield an opaque red crystalline crust, which Fritzsche regarded as $V^2O^5, H^2O, 2SO^3$ (*Jahresb.* 1851, 35), but which, according to Gerland, is an impure anhydrous bisulphate, $V^2O^5, 2SO^3$. This *basic sulphate* is, however, more readily obtained by heating the normal salt ($V^2O^5, 3SO^3$) at the temperature of melting lead, until sulphuric anhydride ceases to be expelled. Thus prepared, the basic sulphate is a red crystalline mass, deliquescent in moist air to a brown solution, which, on dilution with water, yields a precipitate of vanadic oxide.

Dialysis of a Solution of Vanadic Acid in Sulphuric Acid.—1. When a solution of V^2O^5 in hot sulphuric acid is diluted with water, and dialysed into water, sulphuric acid at first diffuses out rapidly, and a solution is left in the dialyser, containing vanadic acid and sulphuric acid in the proportion of 3 molecules of the former to 1 molecule of the latter. If the diffusion be continued for some time, the dialysed product contains vanadic acid and sulphuric acid in the proportion of 2 molecules to 1 molecule.

2. When a solution of V^2O^5 in cold sulphuric acid is dialysed into water, the sulphuric acid diffuses out, and vanadic acid separates in the dialyser, whilst the liquid

contains sulphuric and vanadic acids in the proportion of 1 molecule to 1.32 molecule. This difference in the two cases appears to be due to the fact that the cold solution contains only a molecular compound of V_2O_5 and H_2SO_4 , whilst the solution prepared by the aid of heat contains the atomic compound $V_2O_5(SO_4)_3$.

Double Sulphates.—Calculated quantities of $V_2O_5(SO_4)_3$ and K_2SO_4 dissolved in water and mixed, yield, on heating to a blood heat, amber-coloured crystals, grouped in transparent or turbid nodules. The crystals have the composition $K_2O, V_2O_5, 2SO_3 + 6H_2O$, and are decomposed by water, with liberation of vanadic acid as a brown mud containing some potassium.

Ammonium sulphate forms a double salt similar to the potassium double salt, having the composition $(NH_4)_2O, V_2O_5, 2SO_3 + 4H_2O$. It crystallises in nodular masses formed of needles grouped together, and dissolves in water without separation of vanadic acid. The sulphates of sodium and magnesium do not form double salts with vanadic sulphate.

Metavanadic Acid, VO_3H .—Gerland (*Chem. News*, xxxiv. 2) prepares this acid by mixing a cold saturated solution of copper sulphate with a strong solution of ammonium chloride in large excess, then adding ammonium vanadate in saturated solution till a permanent precipitate appears, and slowly heating the mixture to 75° , when gold-like scales of vanadic acid form and continue to do so for some hours. The precipitate is collected, treated with dilute sulphuric and sulphurous acids, then washed with water and dried, but it still retains traces of ammonia. Metavanadic acid may also be obtained by precipitating ammonium vanadate with a copper salt, separating the precipitated cupric vanadate, and warming the remaining solution. The acid thereupon separates and may be purified from copper by hydrochloric acid.

Metavanadic acid is highly hygroscopic, suffers no change at 150° , but loses its water at higher temperatures. The filtrate from the copper vanadate, if kept for ten days, remains clear on boiling. The original liquor evaporated in a thin layer at low temperature, leaves a crystalline residue, forming with cold water a clear solution which, when heated to 75° , deposits metavanadic acid in scales.

Vanadates. The following vanadates have been examined by J. A. Norblad (*Ber.* viii. 126).

K_2O, V_2O_5 . . . lenticular crystals.	$K_2O, 3V_2O_5 + 6H_2O$. . insoluble.
$K_2O, V_2O_5 + 2H_2O$. capillary needles.	Na_2O, V_2O_5 .
$2K_2O, V_2O_5 + 3H_2O$. monoclinic.	$Na_2O, V_2O_5 + 4H_2O$.
$K_2O, 2V_2O_5 + 4H_2O$ orange red.	$2Na_2O, 3V_2O_5 + 9H_2O$.
$2(K_2O, 2V_2O_5) + 7H_2O$ laminæ having a golden lustre.	$Na_2O, 3V_2O_5 + 9H_2O$.
$K_2O, 3V_2O_5$.	$Li_2O, 2V_2O_5 + 9H_2O$.
	$(NH_4)_2O, 3V_2O_5$. v. Hauer's salt with $6H_2O$ (v. 990) was not obtained.

Ammonium Vanadate.—This salt, when precipitated by ammonium chloride from a solution of sodium vanadate, is obtained pure and free from fixed alkali, whereas when a potassium salt is used, a certain portion of potassium vanadate always goes down with the precipitate (Gerland, *Chem. News*, xxxvi. 29).

The reactions of ammonium vanadate with various organic substances of technical importance have been examined by R. v. Wagner (*Dingl. pol. J.* cccxiii. 631).

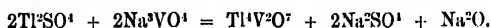
With *tannin-solution* this salt forms a blue-black precipitate, which remains suspended in the liquid for several days, making it like ink. A similar precipitate is formed with *gallic acid*, but it settles down more quickly. *Pyrogallol* forms no precipitate, but a deep black-blue liquid excellently adapted for use with steel pens. *Mucdarin* in aqueous solution also forms a deep black liquid with a greenish tinge; *catechol* reacts in like manner. *Hæmatoxylin* yields a deep black-blue liquid, which may be used as ink. With solution of *logwood-extract* and ammonium vanadate, a fine black colour may be produced on wool or silk, by the usual dyeing process for wood- or chrome-black, the chromate being replaced by vanadate. Extract-solutions of *Brazil-wood* produce with the vanadate at boiling heat a black-brown dyeing liquid; pure *brazilin* acquires only a dark violet colour. A decoction of *fustic* forms with the vanadate a blackish-green ink. The vanadate solution produces no coloration with phenol, salicylic acid, resorcinol, quinol, caffeine, eosin, or fluorescein. Lastly, Wagner recommends ammonium vanadate for detecting the addition of tannin to red wines, which when thus adulterated produce inky liquids, whereas with pure wines only red-brown colorations are obtained.

Silver Vanadates.—An octovanadate, $Ag^{12}V_8O_{28}$, is obtained as a dark yellow precipitate on adding silver nitrate to a solution of the corresponding sodium salt.

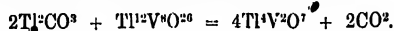
Sp. gr. = 5.67 at 18°. One part of it dissolves in 21,414 pts. water at 14°, in 13,617 pts. at 160°. The *pyrovanadate*, $\text{Ag}^4\text{V}^2\text{O}^7$, is obtained, likewise by precipitation, from the corresponding sodium salt.

Sodium Vanadates.—The *octovanadate*, $\text{Ag}^{12}\text{V}^8\text{O}^{28}$, with 4 or 12 mol. H^2O , is formed by fusing 6 mol. sodium carbonate with 4 mol. vanadium pentoxide. On dissolving the melt in water, evaporating the solution to a syrup, and leaving it at rest for some time, the salt is obtained as a crystalline mass slightly soluble in cold water (Carnelley).

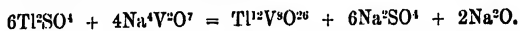
Thallium Vanadates. (Carnelley, *Chem. Soc. J.* xxvi. 323).—These salts for the most part differ greatly in character from the phosphates of the alkali-metals and of thallium, and are more nearly allied to the vanadates of silver and lead. *Thallium orthovanadate*, Tl^2VO^4 , is formed by fusing together at a moderate heat 3 mol. thallium carbonate and 1 mol. vanadium pentoxide, a red mass being thereby produced, which yields a light brown powder. The salt has a sp. gr. of 8.6 at 17°; it is but slightly soluble in water, although it is the most soluble of all the thallium vanadates. It dissolves in 999 pts. water at 15°, and in 574 pts. at 100°. The *pyrovanadate*, $\text{Tl}^4\text{V}^2\text{O}^7$, is obtained as a light yellow precipitate on mixing the cold solutions of thallium sulphate and sodium orthovanadate, the liquid at the same time becoming strongly alkaline:



The same salt is formed by fusing 2 mol. thallium carbonate with 1 mol. V^2O^5 , or 2 mol. thallium carbonate with 1 mol. thallium octovanadate:

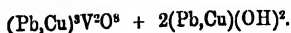


Thallium pyrovanadate is a light yellow or cream-coloured powder; the sp. gr. of the precipitated salt at 18.5° is 8.21, that of the salt obtained by fusion is 8.812 at the same temperature. 1 pt. of the salt dissolves in 4,996 pts. water at 14°, and in 3,840 pts. at 100°. *Thallium octovanadate*, $\text{Tl}^{12}\text{V}^8\text{O}^{28}$ or $6\text{Tl}^2\text{O} \cdot 4\text{V}^2\text{O}^5$, analogous to Fleitmann and Henneberg's sodium octophosphate (v. 537), is prepared by boiling a solution of sodium pyrovanadate, leaving it to cool, and then adding a cold solution of thallium sulphate as long as a precipitate is formed. It has a great resemblance to silver chloride, but changes on standing, especially if the precipitate be stirred, into a fine dense yellow powder. The filtrate contains caustic soda, so that the reaction may be represented by the equation:



Sp. gr. 8.59 at 17.5°. 1 pt. of the salt dissolves in 3,406 pts. water at 8.59°, and in 3,533 pts. at 100°. *Thallium decavanadate*, $\text{Tl}^{12}\text{V}^{10}\text{O}^{31}$, is formed on adding thallium sulphate to a boiled and cooled solution of sodium pyrovanadate containing an excess of vanadium pentoxide, and separates as a white precipitate, becoming light yellow on addition of a larger quantity of thallium sulphate. The filtrate contains free soda. The salt forms a light yellow powder, having a sp. gr. of 7.86 at 17°. One part of it dissolves in 9,372 pts. water at 11° and in 3,366 pts. at 100°. *Thallium metavanadate*, TlVO^3 , obtained by fusing 1 mol. thallium carbonate with 1 mol. V^2O^5 , is a dark-coloured, scaly, crystalline mass, yielding a slate-grey powder. Sp. gr. 6.019 at 17°. One part dissolves in 11,534 pts. water at 11°, and in 4,756 pts. at 100°. *Tetradecavanadate*, $\text{Tl}^2\text{V}^{14}\text{O}^{41}$. When thallium sulphate is added to a solution of ammonium metavanadate, a yellowish precipitate is formed, which gradually becomes darker, and changes on standing into a dirty white crystalline powder, which on addition of more thallium sulphate, or spontaneously after some time, acquires a reddish colour. This product is the tetradecavanadate. The same salt is obtained on adding an excess of thallium sulphate to a solution of the decavanadate.

NATIVE VANADATES. *Mottramite*, a basic vanadate of copper and lead, occurring in crystalline or amorphous incrustations on the keuper sandstone of Alderley Edge and Mottram St. Andrews, Cheshire, has been analysed by H. E. Roscoe (*Proc. Roy. Soc.* xxv. 111). The layers, which are for the most part only 3–4 mm. thick, and the more rarely occurring lumps of the size of a walnut, are either red-brown, opaque, and massive, or are made up of very small needles, black by reflected, yellow by transmitted light. The direct results of analysis are given under Nos. 1 and 2, the mean under No. 3; No. 4 gives the corrected values, after deduction of adventitious constituents, and No. 5 the values calculated from the formula



	V ² O ⁵	PbO	CaO	FeO,ZnO,MnO	CaO	MgO	H ² O	H ² O(°)	SiO ²	
1 (found)	16.78	50.49	16.72	2.52	2.61	0.37	3.63	0.22	0.87	= 97.21
2 "	17.49	51.45	18.48	2.52	1.64	0.16	3.63	0.22	1.25	= 96.84
3 (mean)	17.14	50.97	19.10	2.52	2.13	0.26	3.63	0.22	1.06	= 97.03
4 (corr.)	18.87	56.12	21.02	—	—	—	3.99	—	—	= 100
5 (calc.)	18.74	57.18	20.39	—	—	—	3.69	—	—	= 100

(°) Hygroscopic.

Another vanadate of copper and lead, called *Psittacinite*, occurs in fine-green, occasionally botryoidal crusts on quartz, accompanying gold, cerussite, copper-pyrites, and brown hæmatite, in several mines of the Silver Star District, Montana, especially the Iron Road and New Career mines. Its analysis by F. A. Genth (*Sill. Am. J.* [3], xii. 35) leads to the formula $3(3\text{PbO}, \text{V}^2\text{O}^5) + 3\text{CuO}, \text{V}^2\text{O}^5 + 6(\text{CuO}, \text{H}^2\text{O}) + 12\text{H}^2\text{O}$, the values calculated from which are given below (No. 6):—

	PbO	CuO	V ² O ⁵	H ² O	SiO ²	Al ² O ³	Fe ² O ³	MgO	CuO
1 (found)	41.36	14.34	14.64	7.42	15.13	1.29	2.72	undet.	undet.
2 "	50.17	16.66	19.05	undet.	7.60				
3 "	42.89	14.72	15.87	undet.	10.10	3.83	2.19	6.65	0.15
4 "	27.12	9.75	9.96	undet.	48.84				
5 "	42.38	15.03	15.77	7.25	15.57	4.00			
6 (calc.)	53.15	18.93	19.32	7.58	—	—	—	—	—

Volborthite, a vanadate occurring at Woskresowski, in the government of Perm, Russia, as a crystalline coating on the granules and in the cavities of an argillaceous quartz-conglomerate, has been analysed by Genth (*Zeitschr. f. Kryst.* ii. 12), who refers the analyses (1 and 2), after deduction of impurities, to the formula $(\frac{1}{3}\text{Ba}, \frac{2}{3}\text{Ca}, \frac{1}{3}\text{Cu})^2\text{V}^2\text{O}^5 + 3\text{CuH}^2\text{O} + 12\text{H}^2\text{O}$ (No. 3), closely related to that of psittacinite.

	SiO ²	Al ² O ³	Fe ² O ³	MgO	CuO	CaO	BaO	V ² O ⁵	H ² O(°)
(1)	1.38	4.45	1.77	3.01	34.04	4.29	4.29	13.62	33.15
(2)	1.36	4.78	0.45	1.42	38.01	4.49	4.30	13.69	31.60
(3)	—	—	—	—	38.41	6.77	6.17	19.63	29.02

(°) Determined by difference.

Roscoelite.—This name has been given by J. Blake (*Sill. Am. J.* [3], xii. 31) to a mineral found in a gold-mine at San Francisco, where it serves as a matrix for gold. It occurs in radiating and foliated tale-like masses, filling cavities in a schistose porphyry. It is of a greenish-grey colour, opaque when seen in mass, but translucent in thin splinters. Lustre subvitreous to fatty; hardness about equal to that of tale; specific gravity = 2.902.

Two analyses gave the following results:—

	SiO ²	V ² O ⁵	Al ² O ³	Fe ² O ³	Mn ² O ³	MgO	CaO	K ² O	Na ² O	H ² O
(1)	41.25	28.85	14.34	1.04	1.45	1.96	.61	8.25	0.72	0.94
(2)	—	28.36	13.94	1.23	0.85	2.06	.62	8.87	0.92	1.22
Mean	41.25	28.60	14.14	1.13	1.15	2.01	.61	8.56	0.82	1.08

These numbers lead to the formula $2(\text{Al}^2\text{O}^3, \text{V}^2\text{O}^5) + 2\text{K}^2\text{O}, 9\text{SiO}^2 + \text{H}^2\text{O}$ or $4\text{AlVO}^4 + \text{K}^2\text{SiO}^2 + \text{H}^2\text{O}$, a portion of the alumina being replaced by the sesquioxides of iron and manganese, and a portion of the potash by lime, magnesia, and soda (Roscoe, *Proc. Roy. Soc.* xxv. 109). See also Genth, *Chem. News*, xxxiv. 78; *Chem. Soc. J.* xxxi. 175.

FLUOROXYVANADATES (H. Baker, *Chem. Soc. J.* xxxiii. 388). *Laminar Potassium Fluoroxovanadate*, $6\text{KF}, \text{V}^2\text{O}^5, 2\text{VOH}^2 + 2\text{H}^2\text{O}$, is obtained by dissolving vanadium pentoxide in acid potassium fluoride, the dissolution being attended with rise of temperature, and separates from the liquid on cooling in yellow crystalline spherules made up of groups of small hexagonal tablets. Its aqueous solution has a deep yellow colour.

The *needle-shaped potassium salt*, $3\text{HKF}^2, 2\text{VOH}^2$, is formed on dissolving the preceding salt in warm aqueous hydrofluoric acid, and separates in tufts of long slender needles, which smell of hydrofluoric acid, attack glass quickly, and are decomposed with effervescence by cold sulphuric acid.

Ammonium Fluoroxovanadates are easily formed by dissolving vanadium pentoxide in acid ammonium fluoride. The solution, if rich in vanadium, does not crystallise on standing, but on addition of an excess of hydrogen-ammonium fluoride deposits

faintly yellowish, nacreous, translucent, extremely thin hexagonal laminæ of *Laminar Ammonium Fluorovanadate*. Its aqueous solution, mixed with a larger quantity of hydrogen-ammonium fluoride, yields a light yellow crystalline precipitate of *Pyramidal Ammonium Fluorovanadate*. This salt has a yellow colour, very much like that of potassium rhonchomate, and approximates in crystalline form to the regular octohedron, but its behaviour to polarised light shows that it does not belong to the regular system. By dissolving it in warm hydrofluoric acid, and leaving the solution to cool, *Needle-shaped Ammonium Fluorovanadate*, $3(\text{NH}_4)\text{HF}_2 \cdot 3\text{VOF}_3$, is obtained in light yellow needles or prisms, which smell of hydrofluoric acid when dry, effervesce with cold sulphuric acid, and when laid on glass acquire a reddish colour, with separation of vanadic acid. *Ammonium Fluorohypovanadate*, $2\text{NH}_4\text{F} \cdot \text{VOF}_3$, is obtained by adding hydrogen-ammonium fluoride to vanadium tetroxide prepared by passing hydrogen sulphide into a solution of the pentoxide in hydrofluoric acid. It then separates in clear blue monoclinic crystals, exhibiting the combination $\infty \text{P} \cdot 0\text{P}$. often with an indication of $+ \text{P}$. Axial ratio, $a : b = 0.9653 : 1$. Axial angle, $38^\circ 2'$. The aqueous solution is precipitated by alcohol. The salt is not attacked by cold sulphuric acid.

Zinc Fluorovanadate, $\text{ZnF}_2 \cdot \text{ZnO} \cdot 2\text{VOF}_3 + 14\text{H}_2\text{O}$, is formed on dissolving zinc carbonate and vanadium pentoxide in the calculated proportion in hydrofluoric acid, and separates on evaporation in hard yellow monoclinic prisms, $\infty \text{P} \cdot \infty \text{P} \cdot \infty \text{P} \cdot 0\text{P} \cdot + \text{P} \cdot \infty$, and having approximately the axial ratio $a : b : c = 0.93 : 1 : 0.83$, and the axial angle 46° . On exposure to the air it decomposes slowly, becoming covered with a brown to light red film.

VANILLA. Tiemann and Haarmann (*Ber.* ix. 1297) have found the following proportions of vanillin in different sorts of vanilla: Mexican, 1.32 to 1.86 per cent.; Bourbon, 0.75 to 2.9 per cent.; Java, 1.56 to 2.75 per cent. These vanillas also contain vanillic acid, a small quantity of fat, and a resin having a very faint odour. The benzoic acid, said by former investigators to be present in vanilla, was probably vanillic acid. The aroma of the vanillas above-mentioned is due entirely to vanillin. The West Indian variety called *vanillone* exhibits different characters, its odour strongly resembling that of a dilute solution of piperonal. It contains from 0.4 to 0.7 per cent. vanillin, to which there obstinately adheres an oily substance, probably another aldehyde; the oil absorbed from it by bibulous paper smelt not like piperonal, but like bitter almond oil. The vanillic acid prepared from vanillone was contaminated with another substance, probably benzoic acid. The heliotrope-like odour of vanillone is perhaps due to vanillin mixed with a small quantity of benzaldehyde. The aqueous extract of vanilla pods previously exhausted with ether reduces Fehling's solution, and deposits on boiling a yellow resin: hence it is probable that the water extracts a glucoside which is concerned in the formation of the vanillin.

On the origin of vanilla, its commercial varieties, and their preparation for the market, see *Pharm. J. Trans.*, 1874.

* On the estimation of Vanillin in Vanilla, see p. 306.

VANILLIC or **METHYLPROTOCATECHUIC ACID**, $\text{C}^6\text{H}^4\text{O}^4$ = $\text{C}^6\text{H}^2(\text{CO}^2\text{H})(\text{OCH}^3)(\text{OH})$, and *Isovanillic acid*, $\text{C}^6\text{H}^2(\text{CO}^2\text{H})(\text{OH})(\text{OCH}^3)$. See *Benzoic Acids* (Diox-), p. 289, and *PROTOCATECHUIC ACID*, pp. 1691-1693.

Vanillic acid may be obtained by oxidation of creosol, $\text{C}^8\text{H}^{10}\text{O}^2$ (p. 580). Pure creosol (b. p. 220°) is converted by boiling with acetic anhydride into acetyl-creosol (b. p. 245°); this latter compound suspended in dilute acetic acid is treated with solution of potassium permanganate (1 : 10); and the liquid, filtered from manganese dioxide, is mixed with a slight excess of caustic soda (to decompose aceto-vanillic acid), then concentrated, acidulated, and agitated with ether, which takes up the vanillic acid (Tiemann and Mendelsch, *Ber.* ix. 417).

Alphahomovanillic Acid, $\text{C}^8\text{H}^{10}\text{O}^4$, and its Derivatives (Tiemann and Nagai, *Ber.* x. 201).

Acet-alphahomovanillic acid, $\text{C}^8\text{H}^2(\text{OCH}^3)(\text{OC}^2\text{H}^3\text{O}) \cdot \text{CH}^2 \cdot \text{COOH}$, is formed, together with acetovanillic acid, on adding gradually a warm solution of 50 grams of potassium permanganate in 2,000 c.c. of water to a solution of 15 grams of acetougenol (p. 762) in 20 c.c. of glacial acetic acid. It crystallises in transparent prisms, which dissolve easily in boiling water, alcohol, and ether, and melt at 140° . When heated above its melting point for some time, it gives off acetic acid, and yields alphahomovanillic acid. By prolonged fusion with potassium hydrate, it is converted into protocatechuic acid. Its solution in acetic acid is converted by oxidation with potassium permanganate into acetovanillic acid.

Alphahomovanillic acid, $\text{C}^8\text{H}^2(\text{OCH}^3)(\text{OH}) \cdot \text{CH}^2 \cdot \text{COOH}$, is formed, as above

stated, when a solution of acet-alphahomovanillic acid in soda-ley is heated for some time. It crystallises from boiling water or benzene in distinct hexagonal prisms, which melt at 142° – 143° and dissolve easily in alcohol and ether. Its aqueous solution is coloured green by ferric chloride. The acid forms crystallisable and easily soluble ammonium, sodium, calcium, and barium salts, and sparingly soluble lead, silver, and zinc salts, in which the hydrogen of the carboxyl-group of the acid is replaced by the respective metallic radicles. It appears also to form another class of salts, in which the hydrogen of the hydroxyl in the benzene-residue is likewise replaced, but these are obtained with difficulty. Solutions of the alkali-salts do not reduce Fehling's solution.

Crescol (*homoguaiacol*), $C^6H^3(CH^3)(OCH^3)(OH)$, one of the constituents of beechwood-tar, is formed by elimination of carbon dioxide, when the calcium salt of alphahomovanillic acid is mixed with calcium hydrate and sand, and submitted to dry distillation. It is more easily obtained in the pure state by this process than by treatment of the tar, which yields it only with extreme difficulty.

Alphahomoprotocatechuic acid, $C^6H^3(OH)^2.CH^2.COOH$, is formed when alphahomovanillic acid is heated to 170° – 180° with dilute hydrochloric acid in sealed tubes. It crystallises in brilliant transparent needles, which melt at 127° and dissolve easily in water, alcohol, and ether. It yields well-characterised crystallisable salts by substitution of metallic radicles for the hydrogen of the carboxyl-group. Basic salts also are formed by the further replacement of hydrogen in the hydroxyl-group, but they appear to be unstable.

The calcium salt of alphahomoprotocatechuic acid, when distilled with calcium hydrate, yields homocatechol, $C^6H^3(CH^3)(OH)^2$, a thick, colourless, uncrystallisable liquid which dissolves in water, alcohol, ether, and benzene, and in its chemical properties closely resembles catechol.

VANILLIN, $C^8H^{10}O^3 = C^6.GOH.H.OCH^3.OH.H^2$. *Methyl-protocatechuic Aldehyde* (p. 305).—This compound is a constituent of Siamese benzoin. To prepare it therefrom, 2 pts. of the finely pulverised resin are stirred up to a paste with 1 pt. of slaked lime, and 12 pts. of boiling water are added with constant agitation. The acidulated solution, separated from benzoic acid, yields to ether (together with a little more benzoic acid), vanillin, and a compound which dissolves with yellow colour in alkalis. The vanillin is purified by means of sodium bisulphite. It crystallises remarkably well from light petroleum boiling at 90° . It melts at 81° (Jannasch a. Rump, *Ber.* xi. 1634).

VANILLODIACETONAMINE, $C^{11}H^{16}NO^3$ (Heintz, *Liebig's Annalen*, xciv. 53). This base is obtained by boiling together equal parts of vanillin and acid diacetaminato oxalate in 10 pts. alcohol, whereupon a fine powder separates, consisting of neutral vanillodiace-tonamine oxalate, which may be separated from admixed ammonium oxalate by boiling with a small quantity of water. The free base separated from the solution of this salt by sodium carbonate is a thickish, yellow-green, uncrystallisable oil, which dissolves with yellow colour in ether and alcohol and has a strong alkaline reaction. The *sulphate* forms small thin rectangular or octagonal anhydrous laminae, insoluble in absolute alcohol, slightly soluble in dilute alcohol, more freely in boiling water. The *hydrochloride* forms granular masses composed of slender needles; it dissolves easily in alcohol, and is separated from the solution by ether in small spherical granules destitute of crystalline structure. With platinum chloride it forms a brown-red glutinous precipitate of a *platinochloride*, which dissolves in hot alcohol but does not crystallise therefrom. The *nitrate* forms small geodes of prismatic crystals or rectangular plates, moderately soluble in alcohol, not readily in water. When heated it melts, turns brown, froths up, and gives off yellow vapours. By boiling with strong alcohol it becomes anhydrous and then forms a white powder. The crystallised salt contains 1 mol. water, which is easily expelled at 100° . The anhydrous salt is less soluble in alcohol than the hydrated salt. The *normal axalate* (supra) forms a white powder or yellowish crystalline crusts, slightly soluble in water, insoluble in alcohol and ether.

VANILLYL ALCOHOL, $C^8H^{10}O^3 = C^6.CH^2OH.H.OCH^3.OH.H^2$ (pp. 305, 1692).

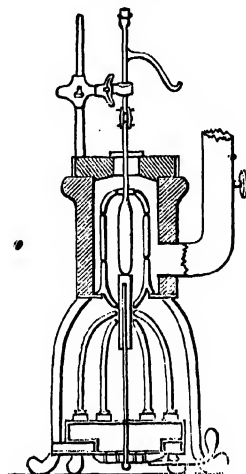
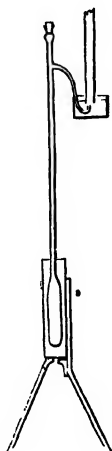
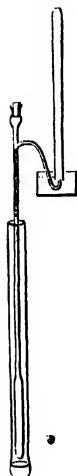
VAPOUR-DENSITY. Numerous methods of determining vapour-densities have recently been proposed, but the only one that need be described in detail is that of V. and C. Meyer (*Ber.* x. 2253). This method consists in dropping a weighed quantity of substance into a heated bulb, and calculating the result from the volume of air displaced. The apparatus used is represented in figs. 50, 51. The bulb is a cylindrical vessel of about 100 c.c. capacity, with a height of 200 mm., to which is

fixed a tube 600 mm. long and 6 mm. diameter, and terminating above in a thimble-shaped enlargement. The side exit-tube, which is 1 mm. diam. and 140 mm. long, is bent at an angle downwards, recurved at the end, and joined to the vertical tube at a distance of 100 mm. from the top. For temperatures up to 300° it is heated in a glass tube 40 mm. diam. and 520 mm. long, which terminates below in a bulb of about 80 c.c. capacity (fig. 50). For higher temperatures the glass tube is replaced by a cylindrical iron vessel (fig. 51), 60 mm. diam. and 240 mm. high, containing melted lead. In this case the bulb must be protected by wire gauze. The mode of working is the following:—The instrument, into which a little well-ignited asbestos has been introduced, is fixed in position in the bath, the end of its fine tube dipping below the water in a small trough in which a graduated tube filled with water stands

FIG. 50.

FIG. 51.

FIG. 52.



inverted. A cork is now inserted into the enlargement at the top of the vertical tube, and the extremity of the exit-tube is watched to see that the temperature in the bulb is uniform. The cork is now taken out, the little tube with the substance is dropped in, and the cork is quickly replaced. The first few bubbles of air are not heeded, but immediately afterwards the inverted tube is placed quickly over the point of the delivery-tube. Very soon the substance is vaporised and displaces air, which issues in a rapid stream of bubbles into the graduated tube. As soon as the gas evolution is over the cork is removed, and the air collected is cooled and measured. The formula given is

$$D = \frac{\text{weight of substance}}{\text{weight of air collected}}$$

(It must, however, be observed that no allowance is made for the volume of the substance.) For temperatures above a red heat the following method is employed (*Ber.* xii. 1112):—The substance is contained in a small cup made from the stem of a Dutch pipe. The vessel in which the determination is made is of glazed porcelain; it is first cautiously heated in an ordinary muffle furnace, and then transferred to a muffle heated by a Perrot's gas-furnace (fig. 52). Before introducing the substance the air in the apparatus is displaced by nitrogen.

For the determination of the vapour-density of substances which attack porcelain at a red heat, Meyer a. Zühlke (*Ber.* xii. 2204) use the following apparatus:—A porcelain tube (glazed inside and outside), 60 c.m. long, is placed vertically in the Perrot's gas-furnace, so that while the centre is heated the two extremities remain cold. Into this tube is inserted the platinum vapour-density bulb. This consists of a cylinder 225 mm. long by 26 mm. diam., to which is attached a platinum tube 400 mm. long by 7 mm. diam.

L. Meyer (*Ber.* xiii. 991) adds a contrivance for dropping the substance after the cork has been inserted. J. Picard (*Ber.* xiii. 1079) has proposed another method of inserting the substance, and modified the arrangement for measuring the air. A new

lead bath for high temperatures is described by Watson Smith (*Chem. Soc. J.* 1880, xxxix).

The following are recently proposed modifications of Hofmann's apparatus (vi. 1127):

Grabowski (*Ber.* viii. 1437) uses naphthalene as the heating medium. Engler (*ibid.* ix. 1437) modifies the apparatus in such a manner as to avoid the occasional stoppage of the outlet tube. Hofmann (*ibid.* 1304) also has modified his apparatus, so as to diminish the risk of cracking the tubes and obviate the necessity of having the inner one graduated. Brühl (*ibid.* 1368; *Monit. scient.* Jan. 1872, 14; *Ber.* xii. 197) uses an inner tube 1.5 mm. long, and to eliminate the tension of mercury-vapour heats the column to the required temperature, notes the height, leaves it to cool, then introduces the substance, and heats it again to the same temperature. Muir a. Sugiura (*Chem. Soc. J.* xxix. 140) insert short glass tubes into the india-rubber disc, to allow free egress to the mercury during the heating. Victor Meyer (*Ber.* ix. 1216; *Monit. scient.* Jan. 1878) uses fusible metal in a bulb with a curved outlet-tube attached to the bottom. His experiments were all made in the vapour of boiling sulphur. Perrenoud (*Liebig's Annalen*, clxxxvii. 77) heats the bulb in an oil-bath, while Knecht (*ibid.* ccii. 31) and Græbe (*Ber.* xi. 1646) use a bath of boiling phosphorus pentasulphide. Frerichs (*Liebig's Annalen*, clxxxv. 199) uses an inverted flask and brings the outlet through the bottom of the bath. Goldschmidt a. Ciamician (*Ber.* x. 641; *Monit. scient.* Jan. 1878) use mercury with the simpler bulb of V. Meyer, but add a small side-tube to the outlet. V. Meyer (*Ber.* x. 2068) modifies the shape of the bulb and heats it in a tube of sufficient length for the upper part to serve as a condenser. Thorpe (*Chem. Soc. J.* 1880, xxxvii. 147) makes the Hofmann apparatus much stronger and more compact, and controls the level of the mercury in the trough by means of a tube passing through the bottom and connected with a movable reservoir. Bell a. Teed (*Chem. Soc. J.* xxxvii. 576) eliminate the atmospheric pressure in Hofmann's apparatus by attaching a side-tube, sealed at the top, which serves as a barometer.

Modifications of Dumas' method (v. 368) have been described by Habermann (*Liebig's Annalen*, clxxxvii. 341) and by Pettersson a. Chatrand (*Ber.* xiii. 1191).

Roscoe (*Proc. Roy. Soc.* xxvii. 426) determines the vapour-densities of high-boiling substances, such as the chlorides of lead and thallium (pp. 1170, 1920), by volatilising them in a long-necked flask of glazed porcelain heated to bright redness in a muffle, the temperature of the flask being estimated calorimetrically by means of platinum weights, likewise introduced into the muffle, and the result checked by the simultaneous heating of a second flask containing mercury.

Pfaundler (*Ber.* iii. 825; xii. 165) describes a method based on the increased tension of the air in an elongated bulb, consequent on the application of heat after the introduction of the substance under examination. Another method, depending on the same principle, is described by Dulong (*Compt. rend.* lxxviii. 536). Hofmann (*Ber.* xi. 1684) proposes to heat the weighed substance over mercury in the closed limb of a V-tube; he also describes a method based on heating the substance in a partially exhausted tube.

An acoustic method of determining vapour-densities, founded on the tone produced in a tube filled with the vapour, as compared with that produced in the same tube filled with air, has been proposed by H. Goldschmidt (*Ber.* xiii. 770).

Alleged Dissociation of Elements at High Temperatures.—From experiments on the vapour-densities of chlorine, bromine, and iodine at high temperatures made by their method above described, V. and C. Meyer (*Ber.* xii. 609, 1195, 1282) inferred that these elements undergo dissociation at high temperatures, the densities of their vapours being reduced to $\frac{2}{3}$ of their normal values. This result appears to be established in the case of iodine, but in that of chlorine it has been admitted by V. Meyer himself to be due to some unexplained experimental error. See Carnelley (*Ber.* vii. 1836); Seelheim (*ibid.* 2066); Lieben (*ibid.* 2259); Crafts (*Ber.* xiii. 423, 776); V. Meyer (*ibid.* xii. 2202; xiii. 813, 1010, 1103); Meier a. Crafts (*Ber.* xiii. 851); Naumann (*ibid.* 1050); Troost (*Compt. rend.* xci. 54); Berthelot (*ibid.* 77); Crafts (*Ber.* xiii. 1316); Deville a. Troost (*Compt. rend.* xci. 83); further, *Chem. Soc. J.* 1880, xxxviii. 214, 431–434, 606, 646, 788.

J. T. B.

VARISCITE. This aluminic phosphate from Massbach, in Saxony, described by Breithaupt as amorphous (v. 994), is, according to Petersen (*Jahrb. f. Min.* 1871, 353), crystalline, and contains:

P ₂ O ₅	Al ₂ O ₃	Fe ²⁺ O ³ (¹)	CaO	MgO	H ₂ O
44.05	31.25	1.21	0.18	0.41	22.85 = 99.95

(¹) With Cr²⁺O³.

These numbers agree with the formula Al²⁺O³.P₂O₅ + 5H₂O, which is also that of turquoise.

A mineral from Montgomery County, Arkansas, hitherto regarded as peganite, has been recognised by A. H. Chester (*Sill. Am. J.* [3], xiii. 295; xv. 207) as variscite. It occurs in quartz, so intimately intergrown that it cannot be completely separated. It is emerald-green, bluish-green, or colourless, sometimes apparently amorphous, but occurs also in radio-fibrous spherules, and even in rhombic crystals 3 mm. in size, and exhibiting the combination $\infty P . \infty \bar{P} \infty . \infty \bar{P} \infty . OP$. Angle $\infty P : \infty P = 114^{\circ} 6'$.

Analyses.—1. Amorphous variety. 2. Crystalline in both cases after deduction of quartz. 3. Values calculated from the formula $Al_2O_3.P_2O_5 + 4H_2O$:

	P_2O_5	Al_2O_3	H_2O
1.	43.96	32.24	23.80 = 100
2.	44.76	31.46	23.80 = 100
3.	44.80	32.49	22.71 = 100

VATERIA. See **PINEY TALLOW** (p. 1630).

VEGETABLE TISSUES. The chemical study of vegetable tissues has hitherto received but little attention, and no general method, such as is used in mineral analysis, has been applied to their separation and estimation. Such a method has, however, lately been devised by Frémy (*Compt. rend.* lxxxiii. 1136), and the following bodies have been thereby distinguished in the principal tissues of vegetables: *Cellulose bodies* (cellulose, paracellulose, metacellulose), *Vasculose*, *Cutose*, *Pectose*, *Calcium pectate*, *Nitrogenous substances*, and various mineral compounds.

Cellulose Bodies.—In this class are included those bodies which dissolve without coloration in bihydrated sulphuric acid, ($SO_4H_2 + H_2O$), producing dextrin and sugar, which are not sensibly altered by alkaline solutions, and resist for a long time the action of strong oxidisers.

By means of the ammonio-cupric reagent, three varieties of cellulose may be distinguished:

(1) *Cellulose*, which dissolves immediately in the cupric reagent, and forms a large part of cotton and of the utricular tissue of certain fruits.

(2) *Paracellulose*, which does not dissolve in the cupric reagent until after the action of acids; it forms the utricular tissue of certain roots and the epidermis of leaves.

(3) *Metacellulose* (fungin), insoluble in the cupric reagent even after the action of acids; found chiefly in agarics and lichens.

In the analysis of vegetable tissue, the first variety of cellulose is determined directly by means of the cupric reagent, the second in the same after being submitted to the action of acids, and the third is dissolved in bihydrated sulphuric acid. When it is not required to distinguish these three bodies, the whole may be dissolved in the sulphuric acid.

Vasculose.—This substance constitutes the larger part of the ducts and spiral vessels; it generally accompanies cellulose in plants, but differs completely from it in composition and properties. It contains more carbon and less hydrogen than cellulose; and is the material which cements the fibres and cells together. It may be said to form the heavy part of woody tissue; it abounds in hard wood and in the stony concretions of pears; the shells of nuts and the stones of apricots contain more than half their weight of vasculose.

Vasculose is insoluble in sulphuric acid, and in the ammonio-cupric reagent, also in alkalis under ordinary circumstances, but when heated with alkalis under pressure it dissolves easily; it also dissolves in oxidising agents. Vasculose can be separated from cellulose by sulphuric acid or by the cupric reagent; but if it is intended to weigh the cellulose, the vasculose must be dissolved in dilute nitric acid.

Cutose constitutes the fine transparent membrane which covers the exposed parts of vegetables. It is insoluble in sulphuric acid, but dissolves in dilute solutions of the carbonates of potassium and sodium; with nitric acid it produces suberic acid. It is separated from cellulose by the cupric reagent, and from vasculose by potash under ordinary atmospheric pressure.

Pectose is insoluble in water, but is rendered soluble and transformed into pectin by dilute acids. It occurs in the utricular tissues of fruits and roots, and is estimated by heating with dilute hydrochloric acid, dissolving in water, and precipitating with alcohol.

Calcium pectate forms part of the membrane which binds the cells together. It is estimated by treatment with dilute hydrochloric acid, which liberates pectic acid in the insoluble state; this is dissolved in potash and reprecipitated by an acid.

The *nitrogenous bodies* and the *inorganic constituents* are determined in the usual way.

The following is a summary of the method of analysis:

Cold dilute hydrochloric acid decomposes the calcium pectate, setting free the pectic acid, which is weighed as alkaline pectate. Boiling dilute hydrochloric acid changes the pectose into pectin, which is precipitated with alcohol. The ammonio-cupric reagent dissolves the cellulose. Hot hydrochloric acid renders paracellulose soluble in the cupric reagent. Sulphuric acid (bihydrated) dissolves the cellulose bodies. Hot dilute potash dissolves the cutose. Potash under pressure dissolves vasculose. Dilute nitric acid renders vasculose soluble in alkaline solutions.

VELELLA. The blue colouring matter of *Velevlla limbosa* has been examined by A. and G. de Negri (*Gazz. chim. ital.* 1877; 219). It changes rapidly after the death of the animal; is insoluble in ether, chloroform, light petroleum, and carbon sulphide; dissolves sparingly in water, forming a liquid which is turned yellow by heating, red by acids, amethyst-coloured by alkalis. Neutralisation of the alkali by an acid does not restore the blue colour. This colouring matter is totally distinct from that of murex and that of the aplypsie, and is spectroscopically distinguished therefrom by the complete absence of absorption-bands.

VENERITE. A copper ore, resembling chlorite in appearance, from the Jones mine, near Springfield, Berks County, Pennsylvania. It is usually very impure, but selected portions showed under the microscope thin transparent laminae mixed with quartz and magnetic iron ore. When separated as completely as possible from these substances it gave by analysis (after deduction of 6.22 per cent. sand):

SiO ²	Al ² O ³	Na ² O ²	FeO	MgO	CuO	H ² O
30.73	14.67	5.35	0.20	18.55	17.58	12.83 = 100

These numbers lead to the oxygen-ratio RO : R²O³ : SiO² : H²O = 3 : 4 : 6 : 4; but the homogeneity of the substance is open to some doubt (T. Sterry Hunt, *Jahrb. f. Min.* 1877, 837).

VERATRIC ACID, C⁹H¹⁰O⁴ = C⁹H³(CO²H)(OCH³)¹(OCH³)².—*Dimethylproto-catechuic acid.* See pp. 991 and 1691–1693.

VERATRUM ALKALOIDS. A. From the seeds of *Veratrum Sabadilla*.—The following bases from sabadilla seeds have been examined by Wright a. Luff. (*Chem. Soc. J.* xxxiii. 338): 1. Cevadine, C³²H⁴⁶NO³, identical with the base called veratrine by Merck (v. 996), and by Schmidt a. Köppen (*Ber. ix.* 1115). 2. Veratrine, identical with the base so named by Couerbe (*Ann. Chim. Phys.* [2], lii. 352). 3. Cevadilline, called *Sabadilline* by Wergelin a. Dragendorff (*Jahresh. f. Pharm.* xxxvii. 94). This alteration of the names of the three bases is made in accordance with their products of saponification, veratrine being thereby converted into veratric acid; cevadine and cevadilline into cevadic acid (i. 843).

Preparation.—The sabadilla seeds were exhausted with alcohol holding in solution 1 per cent. tartaric acid; and the concentrated extract, freed from resin by precipitation with water, was treated with sodium carbonate and ether to dissolve out the alkaloids, which were then redissolved in aqueous tartaric acid, and again taken up by addition of sodium carbonate and agitation with ether. The ethereal solution, mixed with benzolin, left on evaporation a syrupy mass, in which crystals ultimately formed; and these crystals, mixed with viscid matter, were stirred up with a few drops of alcohol, then well drained and slightly washed with alcohol on a vacuum-filter, and finally purified by two or three crystallisations from hot alcohol. They then melted at 205° (like Merck's veratrine), and were converted by saponification into cevadic acid; for this reason, as above mentioned, Wright a. Luff designate the base thus obtained as *cevadine*. The syrupy mass from which the crystals had separated yielded by saponification a mixture of cevadic and veratric acids.

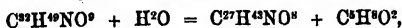
This syrupy mass is only partially soluble in ether; and on dissolving the residue left by ether in tartaric acid, reprecipitating with sodium carbonate, rapidly agitating the precipitate with ether, and repeating this treatment, cevadilline is obtained.

The ethereal solution of the syrupy mass (*infra*), again mixed with benzolin, deposits on standing a syrup, still containing a few crystals of cevadine; and the solution of this syrup in dilute sulphuric acid yields, on addition of ammonia, a precipitate of veratrine (Couerbe's), which may be purified by conversion into the sparingly soluble nitrate and then into the crystalline sulphate.

Twenty pounds of sabadilla seeds yielded from 60 to 70 grāms of crude alkaloids, from which were obtained 9 g. cevadine, 6 g. veratrine, and 3 g. cevadilline. The chief bulk of the basic product is uncrystallisable, and consists most probably of a mixture

of these three alkaloids. Weigelin's sabatrine and sabadilline (vii. 1063) were not found in the mother-liquors.

Cevadine, $C^{27}H^{46}NO^6$ (Schmidt a. Köppen's *Veratrine*), melts at 206° and becomes opaque on exposure to the air, but without losing weight. Its salts are mostly uncrystallisable, but the *aurochloride*, $C^{27}H^{46}NO^6, HCl, AuCl^3 + 2H^2O$, crystallises readily from hot alcohol, and gives off its water at 100° . Cevadine heated with water, or better with alcoholic soda-ley, is decomposed as represented by the equation,



into a white base called *cevine*, and methylcrotonic acid, agreeing in its melting point (64° – 65°) and mode of decomposition by heating with potash, with the methylcrotonic acid of Fränkland a. Duppa (vi. 828), and with the acid called *cevadie acid* by Couerbe and by Pelletier a. Caventou (*Ann. Ch. Phys.* [2], xiv. 69).

To isolate the *cevine*, the acid liquid left after distilling off the volatile acid was filtered from resinous matter, rendered alkaline with caustic soda, and shaken with fusel-oil. The filtered fusel-oil extract left on evaporation a brownish varnish, which dissolved in acetic acid, leaving resinous flakes. The filtrate from these treated with soda and fusel-oil (after fractional precipitation to remove colouring matter), yielded *cevine* in the form of an amber-coloured varnish, melting at 45° , perfectly soluble in acids, easily soluble in alcohol and fusel-oil, sparingly in chloroform, nearly insoluble in ether. Neither the base nor its salts were obtained in the crystalline state, but on adding potassio-mercuric iodide to its solution in acetic acid, white flakes were precipitated, having, when dried at 100° , the composition $C^{27}H^{33}NO^4, HI, HgI^2$.

Cevadine heated at 100° with benzoic anhydride yields benzoyl-cevadine, $C^{27}H^{46}(C^7H^5O)NO^6 + 1\frac{1}{2}H^2O$, which crystallises from ether (cevadine does not), melts at 170° – 180° , and forms an *aurochloride* containing $C^{27}H^{33}NO^6, HCl, AuCl^3$. The formation of this benzoyl-compound shows that cevadine contains a hydroxyl-group, and as this base is converted by saponification into methylcrotonic acid:



its constitution may be represented by the formula:



which is closely related to that of pseudaconitine (p. 1695)

Veratrine, $C^{27}H^{32}NO^{11}$ (Couerbe's), is always amorphous, and melts after purification with ether at 180° (corr.). Its *gold-salt*, $C^{27}H^{32}NO^{11}, HCl, AuCl^3$, is amorphous and shrinks up on drying to a horny mass. The *nitrate* is amorphous. The *hydrochloride* and the *acid sulphate* crystallise, though with difficulty; the latter has the composition $(C^{27}H^{32}NO^{11})H^2SO^4 + 10H^2O$, but has not been obtained quite free from the normal salt. Veratrine is converted by saponification into veratric (dimethylprotocatechuic) acid, $C^8H^7(OCH^3)_2COOH$, and a base called *verine*, which may be extracted by ether in the manner above described for *cevine*, and obtained in the form of a varnish-like mass, which frits at about 95° , melts between 130° and 145° , and forms amorphous salts; its formula is $C^{26}H^{44}NO^6$. From this mode of decomposition it may be inferred that the constitutional formula of veratrine is:



Cevadilline, $C^{34}H^{52}NC^8$, when purified by conversion into tartrate and extraction with ether or benzene, after the liquid has been made alkaline, is amorphous, sparingly soluble in ether, more freely in benzene, during the evaporation of which it separates in amorphous flocks. By saponification it yields a volatile acid, most probably methylcrotonic acid, so that its decomposition may perhaps be represented by the equation $C^{34}H^{52}NO^8 + H^2O = C^8F^8O^2 + C^{26}H^{44}NO^7$, this last formula representing a base which may be called *cevalline*.

The uncrystallisable mother-liquors of the three bases above described probably consist for the most part of *verine* and *cevine*. The isomeric modifications of cevadine (veratrine) mentioned by some chemists* were probably nothing but impure or decomposed cevadine. Weigelin's *sabadilline* (vii. 1063) was perhaps cevadilline;

* Schmidt a. Köppen (*Ber.* ix. 1115) distinguish three modifications of the base which they call veratrine (Wright a. Luff's cevadine), viz. *crystallised*, *resinous*, and *soluble*, to all of which they assign the formula $C^{27}H^{46}NO^6$.

O. Hesse (*Labig's Annalen*, xcii. 186) represents sabadilline (cevadilline) by the formula $C^{34}H^{52}NO^8$, Weigelin's sabatrine by $C^{26}H^{44}O^2$, and Merck's veratrine (cevadine) by $C^{27}H^{32}NO^6$.

The following formulae are given by Tobien (*Pharm. J. Trans.* [3], vii. 808):—Sabadilline, $C^{34}H^{52}NO^8$; sabatrine, $C^{26}H^{44}NO^7$; veratroidine, $C^{34}H^{52}NO^8$ or $C^{26}H^{44}NO^7$; veratrine, $C^{27}H^{32}NO^6$.

and his *sabatrine*, as well as Couerbe's *sabadilline-hydrate*, merely mixtures of decomposition-products (Wright & Luff).

B. Bases from *Veratrum Album*.

The rhizomes of this plant have been examined by several chemists. Weppen obtained from them an alkaloid which he called *veratramarine*, together with *jervic acid*, $C^{14}H^{10}O^{12}$ (vii. 641). *Jervine* was obtained from them by Simon (iii. 443), who assigned to it the formula $C^{30}H^{46}N^2O^8$, afterwards by Mitchell (vii. 709). C. Bullock (*Pharm. J. Trans.* [3], vi. 1009) also found *jervine* in these rhizomes, together with a resin, to the presence of which he ascribed the partial solubility of *jervine* in ether, the similarity of its reaction with sulphuric acid to that exhibited by *veratrine* (*cevadine*), and its physiological action. Pure *jervine*, according to his observations, melts at 196° – 199° , crystallises in prisms resembling *morphine sulphate*, and is completely precipitated from its solution in acetic acid by ammonia and the fixed alkalis.

A. Tobien (*Pharm. J. Trans.* [3], viii. 808) finds in the rhizomes of *Veratrum album* and *V. lobelianum*, of the most various origin, only two alkaloids, viz. *jervine* and *veratroidine*. The rhizomes were soaked in water to which was added 36.8 g. phosphoric acid solution (sp. gr. 1.28) to 2 kg. of solid substance, then repeatedly digested with warm alcohol of 95 percent., and the extracts were evaporated in a vacuum. The residue, diluted with water, deposited a resin, which was dried, mixed with quicklime, moistened with water, and exhausted with alcohol. The extract was then evaporated; the residual *jervine* dissolved in acetic acid, precipitated with sodium carbonate, and redissolved in alcohol, these operations being several times repeated; and finally the *jervine* was converted into nitrate by precipitation with excess of salt-petre and separated therefrom by decomposition with sodium carbonate. By evaporation of its alcoholic solution it is obtained in dazzling white groups of needle-shaped crystals. The same treatment may be employed for the separation of the *jervine* which is precipitated by sodium carbonate from the filtrate of the above-mentioned resin.

Jervine has, according to Tobien, the composition $C^{27}H^{47}N^2O^8$. The formula of its *hydrochloride* is $C^{27}H^{47}N^2O^8 \cdot HCl$; of its *sulphate*, $C^{27}H^{47}N^2O^8 \cdot H^2SO^4$. It is very sparingly soluble in water, readily soluble in alcohol, and dissolves with successively decreasing facility in chloroform, amyl alcohol, benzene, ether, and petroleum. Strong sulphuric acid dissolves it with yellow colour, afterwards changing to yellowish-green; its *hydrochloride* is dissolved by nitric acid with transient rose colour. Its salts are precipitated by potassium nitrate from solutions containing only 1 pt. of salt in 1,200 water.

Veratroidine, $C^{51}H^{78}N^2O^{16}$ or $C^{24}H^{37}NO^7$, is obtained from the filtrates of *jervine* and its salts by supersaturation with caustic alkali and agitation with chloroform. It may be freed from the last portions of *jervine* by addition of nitric acid to its solution in acetic acid, the filtrate being then treated as above. It crystallises from alcohol and ether more readily than *veratrine* (? Merck's or Couerbe's), dissolves to a considerable amount in water, readily in alcohol, ether, and chloroform, less easily in amyl alcohol and benzene, not at all in light petroleum. It is not turned blue by sulphuric acid and sugar (distinction from *veratrine*), and is further distinguished from *veratrine*, *sabatrine*, and *sabadilline*, which it resembles in its reaction with sulphuric acid, by producing a fine but transient red colour with concentrated hydrochloric acid.

The alkaloids of *Veratrum album* have also been examined by Wright and Luff (*Chem. Soc. J.* xxx. 405). The extract obtained with alcohol containing tartaric acid, which was several times used to macerate fresh portions of the root, so as to obtain a solution as concentrated as possible, gave, when fractionally precipitated by sodium carbonate, and fractionally taken up by ether, four different fractions of alkaloid, of which the fraction first precipitated on addition of sodium carbonate, and least soluble in ether, will be called 1, and the most soluble in ether, 4. The fractions 1, 2, and 3 are crystallised, 4 is amorphous (12 kg. of root yielded 50 g. alkaloids, or 0.42 per cent.)

Fraction 3. The base recrystallised from ether was converted by treatment with dilute sulphuric acid into a semi-gelatinous, very sparingly soluble sulphate, which, when decomposed by boiling with sodium carbonate and alcohol, yielded the base, on cooling, in loosely coherent crystals having the composition $C^{27}H^{47}NO^8 + 1\frac{1}{2}H^2O$ (probably $2H^2O$ if quite undecomposed). This base, identical with the *jervine* of Simon and of Will (according to whose analysis, however, it has the composition $C^{30}H^{46}N^2O^8$; see iii. 446), yields a crystallised *hydrochloride* sparingly soluble in water, whether

cold or boiling, still less soluble in hydrochloric acid, more soluble in acetic acid; the nitrate is also but slightly soluble in water. The pure base boils at 237° , but the boiling point is often found lower (231°). Jervine dissolves in strong sulphuric acid with yellow colour, changing through brown to greenish-brown.

Rubijervine, $C^{26}H^{48}NO^2$, is contained as sulphate in the filtrate from the jervine sulphate, and may be separated therefrom by precipitation with caustic soda. It crystallises anhydrous from alcohol, and dissolves in strong sulphuric acid with yellow colour, changing through brown-yellow to brownish-red. The sulphate thus formed is crystalline, easily soluble in cold dilute sulphuric acid, sparingly in cold water. The hydrochloride is crystalline and easily soluble. The free base dissolves in strong sulphuric acid with yellow colour, changing through brown-yellow to brown-red. The aurochloride has the composition $C^{26}H^{48}NO^2, HCl, AuCl^3$.

Pseudojervine, $C^{28}H^{48}NO^2$.—The crude crystals of fraction 1 consist chiefly of this base, which may be separated from adhering jervine by conversion into sulphate, and from rubijervine by subsequent conversion into hydrochloride. Pseudojervine sulphate is sparingly soluble in cold, easily in hot water; whereas its hydrochloride is only slightly soluble in water, either hot or cold, but more easily soluble in dilute hydrochloric acid. Pseudojervine, when quite pure, melts with transient brown coloration at 299° , and reacts with strong sulphuric acid in the same manner as jervine. It is the least soluble in ether of all the crystallised alkaloids of *Veratrum album*.

Veratralbine, $C^{28}H^{48}NO^2$, is an amorphous base contained in fraction 2, together with jervine, a small quantity of pseudojervine, and a still smaller proportion of rubijervine. It is likewise the chief constituent of fraction 4, which, moreover, was once found to contain a small quantity of jervine, and probably also veratrine, inasmuch as it yielded by saponification a small quantity of veratric acid, its powerful sternutatory action being at the same time removed. Cevadic acid was not found in it.

Jervine, pseudojervine, and veratralbine are not saponifiable. The attempt to prepare a benzoyl-derivative from jervine was likewise unsuccessful, although the existence of such a derivative cannot be regarded as impossible. The sternutatory action of *V. album* appears to be due exclusively to veratrine, the amount of which does not exceed 1.25 per cent. of the total alkaloids contained in the root.

C. Bases from *Veratrum viride* (Wright, *Chem. Soc. J.* xxxv. 421).

The rhizome of this plant treated in the manner above described for *Veratrum album* yielded *cevadine* as chief constituent, together with traces of jervine, pseudojervine, rubijervine, veratralbine, and veratrine. The sternutatory action of this rhizome is due to the cevadine. 1 kilogram of the rhizomes of *V. album* and *V. viride* yielded the following quantities of the several bases:

	V. album.	V. viride.
Jervine	1.3	0.2
Pseudojervine	0.4	0.15
Rubijervine	0.25	0.02
Veratralbine	2.2	trace
Veratrine	0.05	trace (less than 0.001)
Cevadine	0.0	0.43
	4.20 g.	0.80 g.

C. Bullock (*Pharm. J. Trans.* [3], x. 186) finds that the resinous substances which separate during the concentration of the extracts of *Veratrum viride* contain the largest portion of the bases existing in that plant. These bases may be separated by treating the resin with milk of lime, concentrating, and exhausting the residue with alcohol, then converting them into acetates and precipitating with caustic soda. In this manner he obtained from a kilogram of the rhizome 6.612 g. of alkaloids; whereas Wright, probably from overlooking the circumstance just mentioned, obtained only 0.8 g.

VERINE, $C^{28}H^{48}NO^2$. A base formed, together with veratric acid, by saponification of veratrine (p. 2099).

VERMICULITE. This name, originally given to a chloritic mineral from Vermont, in North America, containing, according to Thomson, 49.08 per cent. SiO_2 , 7.28 Al_2O_3 , 13.12 FeO, 16.96 MgO, and 10.27 water (v. 997), has been extended by J. P. Cooke (*Phil. Mag.* xlvii. 241; 7, 135) to a family of hydrous silicates, including Culsageeite, Hallite and Jeffersite. These minerals, when heated,

swell up enormously, like alum and borax, in consequence of the escape of their water of crystallisation, after which they undergo complete disintegration.

Analyses. 1. *Sterlingite*, from Massachusetts, a mineral nearly related to *Damourite*, and differing therefrom only in the angle of the optic axes. Yellow to yellowish-white with nacreous lustre; analysed by C. E. Munroe. 2-4. *Celsageeite*, a variety of *Jefferisite* from the Culsagee mine, Macon County, North Carolina; lighter in colour and more easily cleavable than *Jefferisite*. Cooke's analyses differ from those given by Genth (p. 1142) only in the amount of water. 5-8. *Hallite*, a green or yellow micaceous mineral, probably crystallising in the hexagonal system; found in the serpentine of East Nottingham, south of Oxford, Chester County, Massachusetts. The analyses (by C. E. Munroe) 5 and 6 apply to the green, 7 and 8 to the yellow variety. 9. From Lerni, Delaware County, Pennsylvania, sea-green hexagonal plates; analysed by F. A. Gooch. 10. Pelham, Massachusetts; greenish-yellow, resembling *Culsageeite* (Gooch).

	SiO ²	Al ² O ³	Fe ² O ³	FeO	MgO	K ² O	H ² O		Sp. Gr.
1.	43.87	36.45	3.36	—	—	10.86	5.19 =	99.73	2.828 to 2.832
2.	37.58	19.73	5.95	0.58	25.13	—	11.09 =	100.06	
3.	37.43	19.75	5.95	0.58	25.58	—	11.09 =	100.38	2.225
4.	37.10	20.28	5.95	0.58	25.07	—	11.09 =	100.01	
5.	35.97	7.61	8.83	1.13	31.34	0.43	14.32 =	99.63	
6.	35.80	7.29	8.73	1.13	31.56	0.49	14.33 =	99.33	2.398
7.	35.17	7.74	9.76	0.32	31.61	0.56	14.65 =	99.81	
8.	35.34	7.42	9.61	0.32	31.41	0.65	14.91 =	99.86	2.402
9.	38.03	12.93	7.02	0.50	29.64	—	11.68 =	99.80	2.368 to 2.409
10.	41.27	15.19	4.14	—	28.25	—	11.32 =	100.17	2.160 to 2.161

VESBIUM. This name (from Vesbio, an old name of Vesuvius) is given by Scacchi (*Gazz. Chim. ital.* 1880, 21) to a metal which he has discovered in an extremely thin green crust, found coating the fissures of the Vesuvian lava torrent of 1631. The crust being too thin to separate mechanically, the pieces of lava are treated with very dilute hydrochloric acid, which dissolves off the crust, forming a blue solution containing abundance of copper, silica, and other constituents of the lava; the acid solution is evaporated to dryness, heated to 170°, and exhausted with water. The residue consists principally of silica and a vesbium compound, together with a finely divided pulverulent matter which can easily be separated by elutriation; after this has been done, the product is treated with hydrochloric acid, filtered from undissolved silica, and again evaporated to dryness and heated to 170°; and on removing the small quantity of copper present by repeated washing with hot water, the purified vesbium compound remains as a dark-green powder, designated by Scacchi as *vesbine*. This substance is hygroscopic, and when ignited becomes brown without fusing. It is soluble in acids, yielding a green solution; the addition of potash or ammonia to this solution precipitates a ferric compound of vesbium, partly soluble in excess of the precipitant, forming a yellow solution. When *vesbine* is fused with an alkaline carbonate or nitrate, it dissolves with effervescence, forming an alkaline vesbiate soluble in water; on adding an acid to the colourless solution, it acquires a yellow colour similar to that of a chromate, and becoming bluish-green on heating. Alkaline vesbiates give precipitates of various colours with solutions of metallic salts, that with silver being bright red, whilst the zinc salt is greenish. Attempts to obtain potassium vesbiate in the crystalline state were unsuccessful.

On passing hydrogen sulphide through an acid solution of *vesbine*, a brown precipitate is formed, consisting chiefly of sulphur, but containing also small quantities of lead and copper sulphides; the filtrate from this is of a bright blue colour, but becomes colourless on adding excess of ammonia, whilst a brown precipitate is thrown down. When a plate of zinc is immersed in the blue solution, the colour is changed to deep brown, the liquid then appearing almost opaque. Even a very large excess of hydrogen sulphide produces no change in the blue solution. All the vesbium compounds, when fused with microcosmic salt, give a yellow bead tinged with brown in the outer flame, and a green bead in the reducing flame.

VESUVIAN. This mineral occurs on the Rammelsberg, near Deutsch-Tscham-mendorf, south of Strehlen, Silesia, forming veins in a limestone rich in diopside, titanite, and quartz. It contains calcite and diopside microscopically intermixed, but is free from titanite, so that the titanium contained in it must be regarded as isomorphously replacing a part of the silica (E. Schuhmacher, *Jahrb. f. Min.* 1878, 817).

SiO ²	TiO ²	Al ² O ³	Fe ² O ³	Mn ² O ³	FeO	CaO	MgO	H ² O
37.80	1.77	16.28	1.56	0.94	3.11	34.76	2.42	2.29 = 100.93

Crystals of vesuvian occur at Drammen in Norway, lining the walls of cavities

which have been formed in a silurian rock by the weathering of coral residues (W. C. Brögger, *Jahrb. f. Min.* 1876, 661).

The crystallographic constants of a honey-yellow and a black variety of vesuvian from Latium have been determined by J. Strüver (*Zeitschr. f. Kryst.* i. 261; *Jahresb. f. Chem.* 1877, 1307). The vesuvian of Latium occurs only in ejected blocks, mostly well crystallised, sometimes, however, in imperfect crystals and granular masses.

VICIN, $C^8H^{10}N^2O^6$. This substance, which Ritthausen a. Kreusler obtain from vetch-seeds (*J. pr. Chem.* [2], ii. 333), exhibits the following reactions: (1) It is not changed by boiling with baryta-water or with aqueous potash. (2) It dissolves in dilute sulphuric and in hydrochloric acid, the solutions depositing crystals which contain respectively 10·85 per cent. sulphuric acid and 10·02 per cent. chlorine. (3) When solutions of vicin in dilute acids are boiled for some time, they give off small quantities of gas, acquire the odour of decayed fruit, and exhibit the following reactions: (a) With baryta-water in excess, a violet-blue precipitate decolorised on boiling; (b) with ferric chloride and ammonia, a blue coloration, gradually changing to yellow in contact with the air; (c) the solution in sulphuric acid immediately reduces silver nitrate. (4) The solution of vicin in sulphuric acid becomes turbid after heating on the water-bath for twenty or thirty minutes, and on cooling deposits crystals which have the composition $2C^{11}H^{12}N^{10}O^6, 5SO_3$, and exhibit the reactions a, b, c, above described. In ammonia gas this substance becomes purple; in an atmosphere containing moist ammonia the colour changes through blue to bluish-grey; and the substance then forms with water a yellow solution, which, when decomposed by baryta-water, yields a deep yellow pulverulent body not yet examined. On separating the sulphuric acid by the calculated quantity of baryta-water, a colourless solution is obtained, which exhibits all the preceding reactions, but yields on evaporation a soft brownish mass which exhibits none of them. (5) The action of sulphuric acid upon vicin also gives rise to a small quantity of a volatile base and a larger quantity of a syrupy uncrystallisable body. (6) The solution of vicin in hydrochloric acid is precipitated by mercuric, but not by platonic chloride (Ritthausen, *Ber.* ix. 301).

VINYL- or ETHENYL-COMPOUNDS. The pungent liquid called *Vinyl Alcohol*, which Berthelot obtained by agitating acetylene with sulphuric acid and distilling the product with water (vi. 66), appears, from the experiments of Lagermarck a. Eltorkoff (*Ber.* x. 637), not to be an alcohol, but to consist of crotonic aldehyde, C^4H^4O , formed by condensation of acetaldehyde, the first product of the reaction $[2C^2H^3O - H^2O = C^4H^4O]$, and convertible by oxidation with silver oxide into crotonic acid. According to S. Zeisel, on the other hand (*Liebig's Annalen*, xcxi. 366), the formation of acetaldehyde and crotonaldehyde in the experiments of Lagermarck a. Eltorkoff must have been due to the presence of vinyl bromide in the acetylene employed. Vinyl bromide is in fact converted by strong sulphuric acid into crotonaldehyde and a body having the composition $C^2H^4Br^2$, whereas acetylene, after purification by moderate heating with soda-lime and subsequent washing with alcohol and water, is absorbed by sulphuric acid, probably with formation of a sulpho-acid.

The polymerisation of vinyl bromide (b. p. $15^\circ-16^\circ$), observed by Baumann (vii. 1202), is best effected by the most refrangible rays of the spectrum, and more readily when the compound is in the liquid than when it is in the solid state. The condensed product dissolves readily in methyl iodide and most other primary alkyl iodides, also in bromoform, benzaldehyde, and aniline. It is dissolved by strong nitric acid, with formation of a bromo-nitro-compound; reduced by fuming hydriodic acid at 150° .

Vinyl Ethylate or Vinyl-ethyl Oxide, $C^4H^6 = CH^2 = CH.O.C^2H^5$, is formed by the action of sodium at $130^\circ-140^\circ$ on chloroacetal. It is a very mobile liquid which boils at 35.5° ; smells like ethyl oxide, ethylene, and allyl alcohol; dissolves sparingly in water, and, on the other hand, takes up a small quantity of that liquid. Sp. gr. = 0.7625 at 14.5° , referred to water at 17.5° as unity. It unites with chlorine and bromine (most readily when they are diluted with carbon dioxide), forming dichloro- or dibromomethyl oxide (e.g. $CH^2Cl.CHCl.O.C^2H^5$). With small quantities of iodine it thickens, from formation of products of polymerisation or condensation. Moderately dilute sulphuric acid converts vinyl ethylate into aldehyde and ethylsulphuric acid. The same transformation appears to be gradually produced by the action of water, or better by an ammoniacal solution of silver nitrate (Wislicenus, *Liebig's Annalen*, xcii. 106).

Vinyl-anisöl, $C^9H^{10}O = C^8H^7 \begin{matrix} \text{OCH}^3 \\ \text{CH} = \text{CH}^2 \end{matrix}$ See PHENOL-ETHERS (p. 1521).

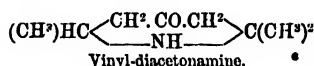
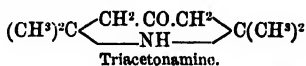
Vinyl-diacetonamine, $C^8H^{13}NO = C^8H^{12}(C^2H^3)NO$ (Heintz, *Liebig's Annalen*, clxxxix. 214; xcxi. 122). The normal oxalate of this base, $C^{16}H^{22}N^2O^6 =$

$(C^6H^{11}NO)^2, C^2H^2O^4$, separates out when 1 pt. of acid diacetonamine oxalate, 12 pts. alcohol, and 4 pts. acetone are heated together for thirty to sixty hours, the ethyl-oxalate of the same base remaining in solution. The formation of vinyl-diacetonamine in this reaction appears to be due to the presence of aldehyde in the acetone employed, the same compound being, in fact, produced in larger quantity by boiling 10 g. acid diacetonamine oxalate with 10 g. aldehyde and 120 g. alcohol in a reflux apparatus for sixty hours. The separated mass (vinyl-diacetonamine oxalate) may be purified by washing with hot alcohol.

Vinyl-diacetonamine separated from the pure oxalate by potash is a colourless, somewhat viscid liquid, which has a burning taste, smells like trimethylamine when cold, like camphor when warm, fumes with hydrochloric acid, and boils almost without decomposition at 199° – 200° . The distilled base turns yellowish after some time. It solidifies at -15° , forming rectangular or six-sided plates or long prisms, which melt at $+27^{\circ}$. It is extremely hygroscopic. The normal sulphate forms microscopic needles, easily soluble in water, sparingly in alcohol, insoluble in ether; it does not lose weight at 100° . An acid oxalate, $C^{18}H^{26}N^4O^{18} = 4C^{18}H^{18}N^4O, 3C^2H^2O^4$, is obtained by dissolving the normal oxalate (*supra*) and oxalic acid in molecular proportions in the smallest possible quantity of hot water, and separates on cooling in short microscopic prisms. Three pts. of this salt and 1 pt. oxalic acid dissolved together in water unite and form a new salt, which loses weight and turns brown at 100° , and is reconverted into the normal oxalate by boiling with alcohol. On evaporating an aqueous solution of 1 pt. of the normal oxalate and 2 pts. *platinic chloride* in a vacuum, exhausting the residue with alcohol and ether, and crystallising it from water, short flat prisms are obtained, often grouped in hexagonal plates, apparently belonging to the rhombic system and having the composition $2C^6H^{11}NO, PtCl^2H^2, 3H^2O$.

Vinyl-diacetonamine is related to triacetonamine in the same manner as acetone to aldehyde, being, in fact, the next lower homologue of triacetonamine, and containing two acetone residues and an aldehyde residue, whereas triacetonamine contains three acetone residues.

The two bodies may perhaps be represented by the following structural formulæ (compare p. 32):



VINYL-TOLUIDINE, C^9H^9N . This base, which Wurtz obtained by heating toluidine with ethylene-chlorhydrin (vi. 1105), is also formed by decomposition of *α*-xethylene-toluidine. See ADDENDA.

VISCUM ALBUM. See MISTLETOE (p. 1331).

VITELLIN. See PROTEIDS (p. 1684).

VIVIANITE. *Native Ferrous Phosphate*. This mineral has been found within and upon the bones of animals on the peat moor of Larchbach; partly in tabular groups of crystals grown together in parallel layers, partly in small needle-shaped monoclinic crystals exhibiting the combination $\infty P \infty R \infty P + P + P \infty$, partly also in radio-fibrous groups. It is blue by reflected light, but by transmitted light it appears almost colourless—merely with a coloured border (F. Becke, *Jahrb. f. Min.* 1878, 79). O. Fraas (*ibid.* 80) found the bones of a saurian from the keuper of Stuttgart converted into vivianite. Vivianite has been found also, in somewhat considerable quantity in the pores of the bog iron ore of Leskowitz, near Friedeg, in Austrian Silesia (Neminar, *Min. Mitth.* 1875, 207).

VOLBOROTHITE. See VANADATES (p. 2092).

VOLCANIC PRODUCTS. The term *Volcano* is commonly used to denote any orifice in the crust of the earth giving vent to materials which afford either direct or indirect evidence of the internal dynamic activity and the inherent heat of our planet. Such orifices are usually found on the flanks or the summit of a conical mound, hill, or mountain. The ejected materials are heated gases, steam, water, mud, dust, scoriæ, and molten rock. The accompaniments are frequently tremors in the earth, and loud noises produced by the concussion of rocks, and the escape of large quantities of gaseous matter in a high state of tension. Volcanic vents vary in size from the smallest *bocche del fuoco* on the flanks of a larger volcanic cone, or the little mud volcanoes of the Caspian, two or three feet in diameter, and the *volcanitos* of New Granada, to the gigantic volcanoes of the Andes, nearly 20,000 feet in height. The commonest form of volcano is that of a conical mound, terminated by a cup-shaped depression or crater, from which a tube descends to unknown depths, and by means of which volcanic products are brought to the surface.

The various kinds of volcanic vent may be conveniently classified as follows:

1. *Extinct Volcanoes*—that is, those which have never been known to be in a state of activity, such as the volcanoes of Auvergne.

2. *Dormant Volcanoes*—that is, those which have been in activity during the historical period, but have given no signs of life for a long term of years, such as Monte Epomeo in the Island of Ischia.

3. *Active Volcanoes*—that is, those which are constantly or at frequent intervals in a state of activity, such as Etna or Stromboli.

4. To these we may add the less common forms of *mud volcanoes*, sometimes called *macalluhe*, or *salses*, which occur in Mexico, on the shores of the Caspian Sea, in Iceland, Sicily, and elsewhere. Hools of boiling mud, which give off quantities of carbonic acid gas, and sometimes also hydrogen and sulphuretted hydrogen, are not uncommon in volcanic countries. *Air volcanoes* (the *volcanitos* of the natives), which eject boiling mud and gaseous products at frequent intervals, were found by Humboldt near Turbaco, in New Granada.

5. *Fumeroli* are small fissures or orifices frequently found within the craters of dormant and active volcanoes, and in recently emitted beds of lava. They give vent to various gaseous products, among which steam usually predominates, and to solid bodies which are carried along mechanically, or volatilised together with the issuing gases. When sulphur and sulphur-products predominate, the fumeroli are called *solfatare*. The *solfioni* of Tuscany are fumeroli by which quantities of boric acid are brought to the surface with the effluent steam. *Mofette* are exhalations of gaseous substances, usually carbonic acid, from hollows in the soil.

6. *Thermal Springs* are closely connected with volcanic phenomena, and their products are properly considered under the head of volcanic products.

In this category may also be placed the *Geysirs* and *Laugs* of Iceland, New Zealand, and North America.

The products—solid, liquid, and gaseous—which are emitted from these various forms of volcanic vent are very varied both as to character and composition, ranging from the commonest elementary bodies to some of the most complex minerals with which we are acquainted. This can scarcely be wondered at when we remember the conditions under which these bodies have been formed. Not only has fire effected a multitude of changes in the composition of volcanic products, but also water and various gases both at high and low temperatures and pressures, acting for short and long durations of time.

I. SOLID PRODUCTS OF VOLCANIC ACTION.

The most plentiful volcanic product is *Lava*, molten rock poured from a crater or from great fissures, and often closely resembling certain iron-furnace slags. Many millions of cubic feet of this substance are often ejected during a single eruption, and we read of a flow of lava which issued from Skapta, in Iceland, in 1783, which was fifty miles long and seven broad. It is important to bear in mind that certain apparently different volcanic products are chemically the same substance in different states of aggregation, or ejected under different conditions of pressure. Thus the compact lava which flows directly from the crater, and the ashes, sand, and scoriae resulting from the same molten lava being blown out of the crater by superheated steam, have precisely the same composition, as the following analyses by Silvestri of substances ejected during the eruption of Etna in 1865 clearly prove:

	Ashes	Sand	Scoriae	Compact Lava
Silica	50.00	49.80	50.00	49.95
Alumina	19.08	18.20	19.00	18.75
Ferrous oxide	12.16	12.42	11.70	11.21
Manganous oxide40	.45	.50	.49
Lime	9.98	11.00	10.28	11.10
Magnesia	4.12	4.00	4.20	4.05
Potash60	.49	.69	.70
Soda	3.72	3.60	3.40	3.71
Water36	.29	.33	.23
Phosphoric acid				
Titanic acid	traces	traces	traces	traces
Vanadic acid				
Ferric oxide				

Moreover, lavas which have been ejected at intervals of many centuries of time have frequently almost precisely the same composition; thus, we may compare one of the lavas of Etna ejected in very ancient times, with the lavas of 1669 and 1866. Microscopic analysis justifies the same conclusion.

Analysis: 1. Very ancient Etna lava. 2. Lava of 1669. 3. Lava of 1866.

	SiO ²	Al ² O ³	FeO	MnO	CaO	MgO	K ² O	Na ² O
1.	49.63	22.47	16.80	0.63	9.05	2.68	0.98	3.07
2.	48.33	16.15	16.32	0.54	9.31	4.58	0.77	3.45
3.	49.95	18.75	11.21	0.40	11.10	4.05	0.70	3.71

The Vesuvian lavas of 1631, 1767, and 1868, as analysed by Haughton, likewise exhibit a close agreement in composition.

SiO ²	Al ² O ³	Fe ² O ³	FeO	MnO	TiO	CaO	MgO	K ² O	Na ² O	H ² O
48.12	17.16	5.69	5.13	1.20	0.22	9.84	3.99	7.24	2.77	0.08
48.20	17.92	5.48	4.75	1.33	0.27	8.97	3.51	7.70	2.61	6.16
46.58	20.00	3.20	5.69	1.07	0.27	9.09	3.16	7.35	2.74	0.32

These lavas also contain small undetermined quantities of phosphoric acid and fluorine; and those of 1767 and 1868 contain in addition traces of fluorine.

Bunsen has divided all volcanic rocks into—

a. *Normal Trachytic*—that is to say, the trachytic rocks which are richest in silica, and represent a mixture of bisilicates of alumina and of potash and soda, while lime, magnesia, and ferrous oxide are almost entirely absent.

b. *Normal Pyroxenic*—that is to say, basaltic and doleritic rocks which contain the smallest quantity of silica, and are basic silicates of alumina and ferrous oxide in combination with lime, magnesia, potash, and soda.

The following is the composition of these two characteristic volcanic products:

	Normal Trachytic	Normal Pyroxenic
Silica	76.67	48.47
Alumina and Ferrous oxide	14.23	30.16
Lime	1.44	11.87
Magnesia	0.28	6.89
Potash	3.20	0.65
Soda	4.18	1.96

It will be at once obvious that the Etna and Vesuvius lavas, the composition of which is given above, closely approximate to the normal pyroxenic type, while obsidian and pumice belong to the normal trachytic type.

Bunsen, moreover, considers that the great number and variety of volcanic rocks containing percentages of silica included between the 76 per cent. of the normal trachytic and the 48 per cent. of the normal pyroxenic, result from mixtures of these rocks in varying proportions, and that 'the great mineralogical and petrographical differences which these rocks present are only consequences of the varying proportions in which the mixtures took place, and of the prevailing physical conditions under which the rocks reached their present situation and assumed their present form.'

The following are examples of some typical lavas, both ancient and modern, of different compositions and from different parts of the world, made in Bunsen's laboratory:

	Hrafninnubrygr, near Krabla, north- east of Iceland. Black Stony Lava	Summit of Elburz	Black Basalt from the Source of the Euphrates	Hekla, Ash of 1845	Compact Grey Volcanic Rock from Kalmastunga, Iceland	Ancient Lava from Hekla
Silica	75.77	69.65	64.76	56.76	53.08	49.37
Alumina and Ferrous oxide	14.14	19.85	22.31	27.47	28.70	28.66
Lime	1.82	4.40	5.13	6.75	9.92	13.01
Magnesia	0.25	2.27	1.91	4.04	5.32	7.52
Potash	2.46	3.83	2.51	2.63	0.61	0.20
Soda	5.56		3.38	2.35	2.37	1.24

Bunsen regards those rocks which contain less than 60 per cent. of silica as *basic*, and those which contain more than 60 per cent. as *acid*. Thus the normal trachytic rock is the extreme acid member, and the normal pyroxenic the extreme basic member. The decomposition of these various rocks, under the influence of heat, air, water, superheated steam, sulphurous acid, hydrochloric acid, and other volcanic products and actions, gives rise to a great number of secondary products.

Elements and Compounds found in Volcanic Products.

Of the fifteen non-metallic elements *twelve* have been found in volcanic products; viz. boron, carbon, chlorine, fluorine, hydrogen, iodine, nitrogen, oxygen, phosphorus, selenium, sulphur, silicon. Of these oxygen and silicon are the most abundant.

Of the fifty-one metallic elements *nineteen* have been found; viz. aluminium, arsenic, caesium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, potassium, rubidium, sodium, thallium, titanium, uranium, zinc, zirconium. Of these aluminium and iron are the most abundant.

The island of Vulcano, one of the Lipari group, has furnished some of the rarest and most complex of volcanic products. To take a single example, a spongy crystalline substance found on the edges of a small fumerole at the bottom of the crater was found to consist of arsenious sulphide, selenium sulphide, boric acid, ammonium chloride, lithium sulphate, thallium alum, caesium alum, rubidium alum, potassium alum. Thus this one substance contained no fewer than seven non-metals and eight metals (see MINERALS, p. 1331).

Native Elements. Few of the elements have been found in the native state among volcanic products. *Oxygen, hydrogen, nitrogen, and chlorine* have been collected from fumeroles. *Sulphur* is found in solfatara in every part of the world, and in the craters of active and dormant volcanoes. It is frequently produced by the interaction of sulphurous acid and hydrogen sulphide. *Selenosulphur*, i.e. indefinite mixtures of selenium and sulphur, has been found in the crater of Vulcano, and in that of Kilauea in the Sandwich Islands. This is the *volcanite* of Haidinger. *Carbon* in the form of graphite was found by Monticelli in an ejected block of Vesuvius, but it is a very rare volcanic product. Native metals, and native metallic alloys, are not found among the products of volcanoes, if we except *metallic copper*, which has been found in the palagonite tuff of the Faroe Islands, and is considered by Bunsen to have been reduced by hydrogen from the chloride.

The following simple combinations of non-metals with metals have been found:

Sulphides. *Red Sulphide of Arsenic, Realgar*, As_2S_2 , occurs in the fumeroles of Vesuvius, and at the solfatara of Puzzuoli. A specimen in the writer's possession from Puzzuoli was raked out of the 'bocca grande,' and was found to consist of microscopic crystals of both the sulphides of arsenic coating a white pumiceous substance. *Yellow Sulphide of Arsenic, Orpiment*, As_2S_3 , Crater of Vulcano. Solfatara of Puzzuoli. *Dimorphite*, the 'Dimorfina' of Scacchi, has been found at the solfatara of Puzzuoli. It is said to contain As_2S_3 , but may perhaps be only a mixture of sulphides. *Iron Bisulphide, Ordinary Iron Pyrites*, FeS_2 , has been found on Vesuvius, at Kriuvik in Iceland, and elsewhere; but it is an uncommon volcanic product. *Nickeliferous Pyrrhotite*, or *Magnetic Iron Pyrites*, FeS_2 , has been found on Vesuvius, having the composition: iron, 58.9; sulphur, 39.9; nickel, 2.6. *Lead Sulphide*, Galena, PbS , has been found in ejected blocks from Vesuvius. *Zinc Sulphide*, Blende, ZnS . Ejected blocks from Vesuvius. *Covellite*, a blue sulphide of copper, CuS , named after Covelli, who first detected it on Vesuvian lavas, is a rare volcanic product. *Dolerophanite* or *Cuprous Sulphide*, Cu_2S , was found by Scacchi as a sublimation produced during the eruption of Vesuvius in 1868. *Chalcocopyrite*, or *Copper Pyrites*, Cu_2S, FeS_2 , has been occasionally found in blocks ejected from Vesuvius, but it is uncommon. It contains copper, 34.5; iron, 30.5; sulphur, 35.0.

Chlorides. *Potassium Chloride, Sylvite*. Fumeroles of Vesuvius and elsewhere. *Sodium Chloride, Halite*. Lavas of Vesuvius and Hekla, and probably existing as a sublimate on the lavas of all volcanoes situated near the sea, shortly after their emission and before rain has fallen. The writer noticed quantities of sublimed salt on the lava of Vesuvius emitted in November 1878. *Lithium Chloride*. Palmieri has detected lithium by means of the spectroscope in the fumerole sublimate of the eruption of Vesuvius of November 1878, associated with ferric chloride. *Calcium Chloride*, found by Bunsen in the sublimate from fumeroles in the Hekla lava of 1845, and by Palmieri in sublimate formed during the eruption of Vesuvius in 1872. *Aluminium Chloride*, Al_2Cl_6 , found by Silliman in a sublimate from the volcano of Kilauea, and by Bunsen in a sublimation from the Hekla lava of 1845, associated

with chlorides of ammonium and iron. *Ammonium Chloride* is a frequent sublimation on lavas, and is often associated with ammonium sulphate and ferric chloride; it has been found at Etna, Hekla, Stromboli, Vulcano, Vesuvius, Kilauea, and elsewhere. When Bunsen visited Hekla, a few months after the eruption of 1845, he observed that the lower part of the lava stream was studded with fumeroles, in which large quantities of beautifully crystallised sal-ammoniac appeared, so that, 'notwithstanding the incessant torrents of rain, hundreds of pounds of this valuable salt might have been collected.' The occurrence of this substance was entirely confined to that portion of the lava stream which had overflowed meadow-land; higher up the stream all traces of the chloride disappeared at the point where vegetation ceased. By submitting a cubic meter of the meadow-land to dry distillation, Bunsen proved that a quantity of ammonia equivalent to 223.3 grams of ammonium chloride was produced. He considers that the ammonium chloride which is found among the fumerole sublimations is derived either from ammonia in the air, which is carried down by rain and converted into chloride by the hydrochloric acid of the fumeroles, or from the distillation of organic matter in the soil over which the lava passes. Daubeny, on the other hand, and Palmieri, consider that, under the conditions of temperature and pressure which must often prevail beneath lava, nitrogen and hydrogen may combine directly. Without attempting to account for the large quantities of ammonia which appear as fumerole sublimations, we may point out that the theory of Daubeny and Palmieri is quite at variance with recent discoveries concerning the dissociation of bodies. The following analysis of a sublimation from the Hekla lava of 1845, taken from fumeroles near the lower part of the stream, was made by Bunsen:

NH ⁴ Cl	4Fe ² O ³ .Fe ³ Cl ³	4Al ² O ³ .Al ³ Cl ³	MgCl ²	CaCl ²	NaCl	KCl	X*
81.68	5.04	3.73	1.69	0.53	1.73	0.95	3.12

* Water and stony residue.

With this we may compare an analysis of an ammonium chloride sublimate from Kilauea, made by Silliman:

NH ⁴ Cl	Fe ³ Cl ³	Al ³ Cl ³	Fe ² O ³	Insol.
65.53	12.14	13.00	8.10	1.23

The composition of these sublimate is not surprising when we remember that hot hydrochloric acid is frequently evolved in abundance from fumeroli in newly ejected lava. The writer found that on passing dry hydrochloric acid over fragments of lava heated to redness in a porcelain tube, the chlorides of iron and aluminium were copiously evolved, while the lava became nearly white and friable, like the masses of decomposed lava frequently met with near hydrochloric acid fumeroli.

Ferric Chloride. Molysite. Fe³Cl³, found by Haussman on Vesuvian lavas in 1819, and by Scacchi in 1855. A common volcanic product, produced by the action of hydrochloric acid on lava. The writer of this article found large cavities containing several hundred square feet of surface, in the lava emitted by Vesuvius in November 1878, completely coated by a sublimate containing a large percentage of ferric chloride, while hot fumes of hydrochloric acid issued from fissures in the sides of the cavities. He also noticed it as a sublimation on the lava emitted from Hekla in February 1878. It is, of course, very deliquescent, and the first shower of rain may remove all traces of it.

Monticelli asserts the existence of *Ferrous Chloride*, FeCl², as a sublimate on Vesuvian lavas, but his statement is not confirmed by Scacchi.

Kremersite, KCl.NH⁴Cl.2Fe²Cl³ + 6H²O, a substance first analysed by Kromers, found as a product of sublimation from fumeroles, contains 55.86 per cent. Cl, 17.65 Fe, 12.32 K, 5.67 NH⁴, and 8.50 water.

Lead Chloride. Cotunnite, PbCl².—Found by Monticelli and Covelli in the crater of Vesuvius, after the eruption of 1822, accompanied by copper chloride and sodium chloride; also by Scacchi and Guiscardi as a product of the eruption of 1855.

Lead Oxychloride, Matlockite, PbCl²PbO, was found as a sublimation-product of a fumerole of Vesuvius after the eruption of 1855.

Hydrated Cupric Oxychloride, Atacamite, Cu²O.Cl² + 4H²O, has been found incrusting Vesuvian lavas of 1820 and 1822. The writer found in the lava of November 1878 cavities lined with microscopic greenish crystals containing copper, in all probability existing as chloride.

Potassium Iodide has been found at Vulcano. The bromide would in all probability be detected if carefully sought for.

Calcium Fluoride has been found in blocks ejected from Vesuvius, and in a few volcanic minerals.

Iron Nitride. Siderazote, Fe³N².—Found by Silvestri on the surface of the hot

lava of Etna (1874); formed artificially by exposing fragments of lava to the alterate action of hydrochloric acid and ammonia at a red heat. See p. 1097.

Oxides. *Black Copper Oxide*, *Melaconite*, or *Tenorite*, CuO , has been found by Semola, Scacchi, and Palmieri on the lavas of Vesuvius, sometimes in crystals. *Red Copper Oxide*, *Cuprite*, Cu_2O , has also been occasionally found on the scorize of Vesuvius.

Ferric Oxide. *Hematite*. Found on the lavas of Etna and Vesuvius in the neighbourhood of fumeroles. *Ferric Hydroxide*, *Gothite*, $\text{Fe}^2\text{O}_3 \cdot \text{H}_2\text{O}$, has been found in the ejected blocks of Somma. *Magnetic Iron Oxide*, *Magnetite*, is a frequent constituent of lavas, as may be shown by the microscopic examination of their sections; it is also found in volcanic sand and in the ejected blocks of Somma. *Magnesian ferrite*, $\text{MgO} \cdot \text{Fe}^2\text{O}_3$, has been found in crystals and laminae near the fumeroles of Vesuvius, particularly those of the eruption of 1855.

	Vesuvius. Old Eruption.	Vesuvius. Eruption of 1855.
Ferric oxide	84.20	85.05
Magnesia	16.00	13.95
Cupric oxide	—	1.01

Periclasite, $\text{MgO} = 93.86$, $\text{FeO} = 5.97$, has been found in clustered crystals in blocks ejected from Somma and Vesuvius.

Spinel, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, found in ejected blocks from Somma and Vesuvius. A specimen from the latter volcano was found to contain 67.46 per cent. Al_2O_3 , 25.94 MgO , 5.06 FeO , and 2.38 SiO_2 .

Titanic Oxide, TiO_2 , both in the form of 'Brookite' and of 'Rutile,' has been occasionally found in the Val del Bove, on the east side of Etna. *Titaniferous Magnetite*, or *Iserine*, $\text{FeO} \cdot \text{TiO}_2 + \text{Fe}^2\text{O}_3$, is frequently found disseminated through lavas, scorize, and tufas; in the eruptive rocks at Arthur's Seat, at Unkel on the Rhine, in basalt, and elsewhere.

Silica is found in the form of quartz in cavities of basalts; occasionally also, according to Monticelli, in the cavities of blocks ejected from Vesuvius (A.D. 79). Silica is also deposited from the *geysirs* of Iceland, New Zealand, and California, and is then known as *Geyserite*. The following analyses show the composition of these deposits:

	Iceland	Iceland	Iceland	New Zealand
Silica	98.00	91.56	88.26	94.20
Alumina	0.50	1.04	0.69	1.58
Ferric oxide	—	0.18	3.26	0.17
Lime	—	0.33	0.29	traces
Soda and Potash	—	0.35	0.22	0.85
Sulphuric acid	—	—	2.49	—
Water	1.5	5.76	4.79	3.06

Silicates. The majority of volcanic products, as indeed of the whole mineral kingdom, consists of silicates of various degrees of complexity. Of these we shall first consider the most simple monosilicates, and afterwards those of more elaborate character and composition.

Calcium Silicate. *Wollastonite*. CaOSiO_2 .—Found in lavas and basalts in various parts of the world.

Pyroxene, or *Augite*, $(\text{CaO}, \text{MgO}, \text{FeO})\text{SiO}_2$, is an essential constituent of many volcanic rocks. The following analyses show the composition of various specimens from different volcanic centres:

	Vesuvius, 1631.	Vesuvius, 1858	Etna, Mt. Rossi	Iceland	Teneriffe	Azores
Silica	48.86	49.61	47.38	49.87	48.05	50.40
Alumina	8.63	4.42	5.52	6.05	4.18	2.99
Ferrous oxide	4.54	9.08	7.80	5.92	23.41	22.00
Magnesia	14.01	14.22	15.29	16.16	9.40	2.40
Lime	20.62	20.83	19.10	22.00	14.96	21.10
Ferric oxide	2.73	—	3.85	—	—	—

Breislakite is a capillary or woolly form of pyroxene, occurring in the lavas of Vesuvius and those of Capo di Bove.

A number of minerals result from the alteration of pyroxene. The following table, from Rutley's 'Study of Rocks,' shows the composition of the principal of these substances.

Name of Mineral	SiO ²	Al ² O ³	Cr ² O ³	Fe ² O ³	FeO	MnO	MgO	CaO	Na ² O	K ² O	TiO ²	H ² O	Authority
Augite	51	3	—	—	6	3	13	24	—	—	—	—	Rammelsberg
Picrophyll	50	2	—	—	6	—	31	1	—	—	—	10	Rose
Pyrrholite	49·5	0·5	—	—	1·5	1	24·5	10·5	—	—	—	12·5	Runeberg
Schiller-spar	43	2	2·5	—	11	0·5	26	2·5	—	—	—	12·5	Köhler
Epidote	46	5·5	—	13	8	—	12·5	9	—	—	—	5	Streng
Mica	43	15	—	—	23·5	—	10·5	1	1	5	—	—	Kjerulf
Uralite	49	1	—	—	25·5	—	12	11·5	—	—	—	1	Rath
Glauconite	51·5	7	—	—	21	—	6	—	2	6	—	6·5	Delesse
Serpentine	41	2	—	—	2	—	42	—	—	—	—	13	Scheerer
Steatite	62·5	—	—	—	1·5	—	31	—	—	—	—	5	Richter
" "	64	1	—	—	—	—	28	—	—	—	—	7	Tengström
Palagonite	42	12·5	—	16	—	—	7	7	2	—	—	12·5	v. Waltershausen
Hæmatite	—	—	—	100	—	—	—	—	—	—	—	—	
Limonite	2·5	—	—	80·5	—	—	—	—	—	—	—	16	Ullmann
Magnetite	—	—	—	69	31	—	—	—	—	—	—	—	
Titaniferous magnetite	—	—	—	22	51·5	2	—	—	—	—	24·5	—	Knop
Ditto	—	—	—	68	30	—	—	—	—	—	2	—	Michaelson

Among these products we may specially notice *Palagonite*, a substance which Bunsen regards as the basis of the basaltic tufas of Germany, France, the Azores, Canaries, Cape Verde Islands, and of the numerous volcanic islands of the Pacific. Dana places palagonite among the hydrous silicates. Bunsen gives it the approximate formula $3\text{RO}, 2\text{SiO}_2 + 3\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{Aq}$. It is met with in an amorphous form in grains and fragments aggregated into a tufa-like rock, and as a constituent of tufa and volcanic conglomerate. The hardness is from 4 to 5. Sp. gr. 2·47–2·7. The colour varies from amber-yellow, through red and brown to black. It melts easily to a black magnetic glass. As to its formation Bunsen remarks, 'Tufas are formed through the action of waters, and often that of heated waters or steam, accompanying an eruption of lavas, on the granulated volcanic rock or volcanic sand; and in this process the ferrous oxide of the pyroxene becomes more or less completely changed to ferric oxide, and water is taken up, and thus palagonite is produced. As the volcanic rock is generally made up of pyroxene and a felspar in very variable proportions, uniformity in such cases of alteration is not possible.' (For analyses see iv. 324.)

Glauconite, a hydrous silicate of iron and potassium, sometimes containing small quantities of silicates of magnesium and aluminium, is found more frequently in sedimentary than in volcanic rocks. It has been found, however, in the latter at Monte Baldo near Verona, and at Berufjord in Iceland. *Celadonite*, in which the iron is in the state of higher oxidation, is found in close proximity at Monte Baldo (see also ii. 846).

	Glauconite, Berufjord	Celadonite, Monte Baldo
Silica	52·04	53·0
Alumina	4·93	—
Ferric oxide	—	28·0
Ferrous oxide	25·54	—
Magnesia	4·26	2·0
Potash	6·03	10·0
Water	5·19	6·0

Hornblende, or *Amphibole*.—Silicates of various monoxides, and of alumina, found in the volcanic rocks of Etna, Vesuvius, Teneriffe, and elsewhere. A specimen from Etna contained silica 40·91, alumina 13·68, ferrous oxide 17·49, magnesia 13·19, lime 13·44. Sometimes contains small quantities of fluorine and of water (see further iii. 167–170).

Magnesium Silicate, *Forsterite*, or *White Olivine* (*peridoto bianco* of Scacchi), has

been found in Vesuvian lavas associated with spinell and pyroxene. Silica 42.41, magnesia 53.30, protoxide of iron 2.33 (iv. 201).

Monticellite, a double silicate of calcium and magnesium, exists in certain lavas of Vesuvius and Somma. It contains silica 37.89, magnesia 22.04, lime 34.92, ferrous oxide 5.61.

Olivine, $(\text{MgO}, \text{FeO})^2\text{SiO}_2$, is a common product of many eruptive rocks.

	Etna	Hekla	Vesuvius	Rifel
Silica	41.01	43.44	40.35	42.21
Ferrous oxide . .	10.06	6.93	12.34	8.91
Magnesia	47.27	49.31	46.70	49.29
Alumina	0.64	trace	—	0.18
Nickel	0.20	0.32	—	—

(See further iv. 201.)

Topaz, a tribasic aluminium silicate having part of the oxygen replaced by fluorine, is said by Monticelli to be occasionally met with as a volcanic product.

Garnet is found in the lavas of Vesuvius, in the volcanic soil near Frascati, and elsewhere in volcanic districts. The iron-alumina-lime garnet is most common. It contains silica 39.93 SiO_2 , 13.45 Al_2O_3 , 10.95 Fe_2O_3 , 3.35 FeO , 1.40 MnO , and 31.66 CaO (ii. 772).

Zircon, ZrSiO_4 , has been found in Vesuvian lavas associated with rhycolite.

Idocrase, or *Vesuvianite*, is found among the ancient ejected blocks of Vesuvius and the dolomites of Somma. It resembles some of the lime-alumina garnets in composition. General formula $6(2\text{RO}, \text{SiO}_2) + 2\text{Al}_2\text{O}_3, 3\text{SiO}_2$. Contains 37.75 SiO_2 , 17.23 Al_2O_3 , 4.43 Fe_2O_3 , 3.79 MgO , 37.35 CaO (v. 998).

Melilite, *Zurite*, *Somerbyllite*, *Humboldtite*, are closely related minerals which are frequently met with in the lavas of Vesuvius and Somma, and in the slags of iron furnaces. Humboldtite contains 40.6 SiO_2 , 10.85 Al_2O_3 , 4.43 Fe_2O_3 , 4.54 MgO , 31.81 CaO , 4.43 Na_2O , 0.36 K_2O .

Biotite, or *Magnesia Mica*, $\text{Al}_2\text{O}_3, \text{SiO}_2 + 3\text{RO}, 2\text{SiO}_2$, is a common constituent of eruptive rocks. It has been found in blocks ejected from Monte Somma, in brilliant crystals. For analyses see iii. 1013.

Common or *Potash Mica* is sometimes found in the blocks ejected from Somma.

Talc, $6\text{MgO}, 7\text{SiO}_2$, is mentioned by Monticelli as a constituent of some of the rocks of Somma.

Sarcinite, the *Analcima carnea* of Monticelli and Covelli, is a volcanic mineral of somewhat rare occurrence, found in ejected blocks, and having a composition somewhat like that of Idocrase (v. 196).

Meionite (called also *Scapolite* and *White Hyacinth*) and *Mizzonite* are minerals resembling each other, found in the rocks of Somma. They are silicates of aluminium and calcium, with a small percentage of sodium silicate (iii. 865).

	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	
Meionite	41.80	30.40	0.46	19.00	2.51	0.86	= 95.03
Mizzonite	54.70	23.80	0.22	8.77	9.83	2.14	= 99.46

Marialite, a mineral found in a volcanic rock called *piperno*, at Pianura, near Naples, contains 59.50 SiO_2 , 20.70 Al_2O_3 , 4.45 Fe_2O_3 , 0.29 MgO , 4.39 CaO , soda 8.90 Na_2O , 1.09 K_2O .

Nephelite, *Davyne*, *Carolinite*, and *Sommite*, very similar minerals, consisting essentially of silicates of alumina and of soda or potash, are found in both ancient and modern lavas, and may be represented by the general formula $4\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{R}_2\text{O}, \text{SiO}_2$ (iv. 30).

Tourmaline, $3\text{R}_2\text{O}_3, \text{SiO}_2 + 3\text{RO}, \text{SiO}_2$; general composition 38 SiO_2 , 36 Al_2O_3 , 8 B_2O_3 ; was found by Brocchi in lava at La Scala and Fosso Grande.

Sodalite with Sodium Chloride, $3(\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{Na}_2\text{O}, \text{SiO}_2) + 2\text{NaCl}$, has been found in trap, basalt, and modern volcanic rocks in Italy, Sicily, and elsewhere (v. 328).

Lapis Lazuli is said to have been found in an ejected block from Monte Somma. Composition somewhat variable (iii. 470).

Hauynite, or *Hauyne*.—Silicates of aluminium and sodium, silicate with sulphate of calcium, has been found among volcanic products at Vesuvius, Auvergne, Monte Vulture, Mount Albano, and the Azores (iii. 15).

Leucite, *White Garnet*, or *Amphigene*, $\text{Al}_2\text{O}_3, 3\text{SiO}_2 + \text{K}_2\text{O}, \text{SiO}_2$, is a mineral confined to volcanic rocks (iii. 583).

	SiO ²	Al ² O ³	Na ² O	K ² O	
Vesuvius (1811)	56.10	23.22	0.57	20.59	= 100.48
Rocca Monfina	56.36	23.15 ₆	0.25	19.31	= 99.07 ₆

Lithia has been detected in Vesuvian leucite.

Leucitophyr is a name given to lavas which contain leucite disseminated through them in grains. Felspar, nephelite, and kaolin occur with the form of leucite (pseudomorphs) as a result of its alteration.

Anorthite, $\text{Al}^2\text{O}^3 \cdot \text{SiO}^2 + \text{CaO} \cdot \text{SiO}^2$, is a common volcanic product of Hekla, Vesuvius, Etna, the Faroe Islands, Iceland, and elsewhere. *Analyses*: (1) From the plains of the Thjorsa, Iceland. (2) From the *Isola dei Ciclopi*, Sicily (for others see i. 308).

	SiO ²	Al ² O ³	Fe ² O ³	MgO	CaO	Na ² O	K ² O	
1.	48.36	30.59	1.37	0.97	17.16	1.13	0.62	= 100.20
2.	41.45	29.83	2.20	0.66	20.83	2.32	1.72	= 99.01

The anorthite from the plains of the Thjorsa is the *Thiorsaite* of Genth; that from the Cyclops Islands, off the east coast of Sicily, is the *Ciclopit* of Santorius von Waltershausen.

Labradorite, $\text{Al}^2\text{O}^3 \cdot 2\text{SiO}^2 + \text{RO} \cdot \text{SiO}^2$ [$\text{R} = \text{Ca}, \text{Na}^2$].—Found in dolerites and basalts in Antrim, Iceland, Italy, Sicily, and elsewhere. It easily undergoes decomposition under the influence of air, water containing carbonic acid, and alkalis. For analyses see ii. 451; vii. 512; viii. 772, 774.

Oligoclase, $2(\text{Al}^2\text{O}^3 \cdot 3\text{SiO}^2) + 2\text{Na}^2\text{O} \cdot 3\text{SiO}^2$.—Found in many volcanic products in Teneriffe and Iceland; in obsidian at Zimapan, in Mexico; in pumice at Arequipa, in Peru, and in various lavas and trachytes. For analyses see iii. 198; vii. 512, 513; viii. 774.

Orthoclase, or *Potash Felspar*, $\text{K}^2\text{Al}^2\text{Si}^6\text{O}^{16}$, or $\text{K}^2\text{O} \cdot \text{Al}^2\text{O}^3 \cdot 6\text{SiO}^2$, and its glassy varieties, *sanidin* and *ryacolite*, occur in trachyte and many other volcanic rocks. *Albite*, or *Soda-felspar*, $\text{Na}^2\text{Al}^2\text{Si}^6\text{O}^{16}$, is found in trachyte in the island of Pantellaria, at Langufjall in Iceland, and many other localities (ii. 620–622; vii. 508–510; viii. 773).

On *Obsidian* and *Pumice* see iv. 169; viii. 1422. Almost any lava may be converted into obsidian by melting and rapid cooling. The writer found that on fusing Giant's Causeway basalt in a gas furnace, and cooling it rapidly, a perfect glass, structureless and transparent under the microscope, was produced. By cooling less quickly, a substance was obtained which was absolutely opaque in the thinnest sections that could be procured.

Krabbite, or *Baulite*, is the obsidian of Mount Krabla in Iceland, and is similar in composition to pitchstones and obsidians. Contains 80.23 per cent. SiO^2 , 12.08 Al^2O^3 , 0.95 MgO , and 7.18 K^2O and Na^2O .

The following silicates, described in this or the preceding volumes of this Dictionary, have also been found amongst volcanic products:

Analcime	Herschelite
Apophyllite	Mesolite
Brewsterite	Natrolite
Chabazite	Okenite
Chondrodite or Humite	Prehnite
Epistilbite	Scolecite
Gehlenite	Thomsonite
Guarinite	Titanite or Sphene
Gismondin,	

Borates. Boron occurs in only a few minerals. *Sassolite*, or native boric acid, occurs abundantly in the crater of Vulcano as a layer upon sulphur; also on Vesuvius, at Krisuvik in Iceland, at Atacama, at Sasso near Sienna, in boracic acid lagoons and soffioni, and elsewhere. Ammonium sulphate often condenses with it in the soffioni. In a hot spring at Krisuvik 1,426 grains of crystallised boric acid have been found.

Ammonium Borate, or *Larderellite*, and *Iron Borate*, or *Lagonite*, are found as incrustations around the lagoons of Tuscany.

Sulphates. *Sulphuric Acid*, mineralogically *Sulphatite*, is noticed below under 'Liquid Volcanic Products.'

Aphthalite, or *Potassium Sulphate*, the 'Vesuvian Salt' of Smithson, called also *Glaserite* and *Arcanite*, has been found in the form of crystals on Vesuvian lava. A specimen gave, on analysis, 71.4 K^2SO^4 , 18.6 Na^2SO^4 , 4.6 NaCl , and 5.4 $\text{CuCl}^2 \cdot \text{NH}^4\text{Cl}$ and Fe^2Cl^6 .

Misenite, or *Potassium-hydrogen Sulphate*, has been found by Scacchi in a hot tufa cavern near Cape Miseno, in the volcanic district around Naples. *Thenardite*, Na^2SO^4 , was found by Scacchi on the scorize of Vesuvius after the eruption of 1855. *Mascagnite*, $(\text{NH}^4)^2\text{SO}^4$, has been found in the fissures of the lavas of Etna, Vesuvius, and Lipari, and in the boric acid lagoons of Tuscany. *Boussingaultite*, a double sulphate of ammonia and magnesia, has also been found in the Tuscany lagoons. *Mirabilite*, $\text{Na}^2\text{SO}^4 \cdot 10\text{H}^2\text{O}$, is abundant in a cavern of the volcano of Kilauea, in the Sandwich Islands. It has also been found on Vesuvius. The *Exanthalose* of Beudant found on Vesuvius contained $\text{Na}^2\text{SO}^4 \cdot 2\text{H}^2\text{O}$. *Gypsum* has been found near fumeroles from which sulphurous acid escapes, also around the mud cauldrons of Krisuvik. *Picromerite*, a magnesium-potassium sulphate, was found on Vesuvius among the salts produced during the eruption of 1855. *Chalcantite*, or *Cyanosite*, $\text{CuSO}^4 \cdot 5\text{H}^2\text{O}$, was observed among the Vesuvian minerals after the eruption of 1855. *Cyanochroite*, the *Cianocroma* of Scacchi, a hydrous sulphate of potassium and copper, was found on the lavas of Vesuvius after the eruption of 1855. *Alunogen*, $\text{Al}^2\text{SO}^6 \cdot 18\text{H}^2\text{O}$, has been found at Pasto in the crater of a volcano, at Krisuvik in Iceland, and at Vesuvius. *Coquimbite*, $\text{Fe}^2(\text{SO}^4)^2 \cdot 9\text{H}^2\text{O}$, was found by Scacchi around the fumeroles of Vesuvius after the eruption of 1855. *Kalinite*, or potash-alum, has been found in Vulcano associated with the *alums* of *Thallium*, *Rubidium*, and *Cesium*. (See MINERALS OF VULCANO, p. 1330.) *Voltaite*, a ferroso-ferric sulphate (v. 1005), has been found at the solfatara of Puzzuoli. *Halotrichite*, $\text{Al}^2(\text{SO}^4)^2 \cdot 18\text{H}^2\text{O}$, in silky fibres, has been found at the solfatara of Puzzuoli and elsewhere. *Alunite*, $\text{AlK}(\text{SO}^4)^2 \cdot \text{AlH}^3\text{O} \cdot 3\text{H}^2\text{O}$, is sometimes found in seams in trachytic and allied rocks, as a result of the alteration of the rock by sulphurous vapours. *Brochantite*, $\text{CuSO}^4 \cdot 3\text{CuH}^2\text{O}^2$, also called *Krisuvigite*, is occasionally met with among volcanic products, e.g. in small quantities at Krisuvik.

Carbonates. It is questionable to what extent we are justified in regarding any carbonate as a volcanic product. The carbonates of copper, calcium, and magnesium have, however, been found in blocks ejected from Monte Somma.

Phosphates. *Apatite*, $\text{Ca}(\text{PO}^4)^3$, containing also chlorine and fluorine, has been found in crystals in ejected blocks on Somma near Pollena. *Copper-Uranite*, $(\text{UO}^2)^2\text{Cu}(\text{PO}^4)^2 \cdot 8\text{H}^2\text{O}$, is mentioned by Monticelli as having been found in green laminae in cavities of certain lavas of Vesuvius, but the statement wants verification.

Proximate Composition of Lava.

The ultimate composition of various typical lavas and mixed volcanic products has already been given (p. 2105). The determination of their proximate constitution is a matter of greater difficulty; the microscopic examination of thin sections of the rock often reveals to us which minerals preponderate, but no more than this.

Haughton and Hull have recently endeavoured to answer, in regard to Vesuvian lavas, the question, 'What is the proportion of each mineral present in the lava, and why does that proportion exist?' The various lavas which have flowed from Vesuvius are mainly made up of nine minerals of known composition, viz. *leucite*, *plagioclase* (triclinic felspar), *magnetite*, *olivine*, *augite*, *hornblende*, *mica*, *nephelite*, and *sodalite*, together with an unknown quantity of a *paste* of unknown composition. This *paste* is the chemical residuum which remains over and above the chemical elements used up in the formation of the minerals. The question of the proximate composition of the lavas has been discussed by Haughton as a branch of the indeterminate analysis, and he assumes as his starting point the following principle: 'Of the numerous solutions possible, that one will occur in nature which involves the largest amount of definite minerals and the least amount of indefinite paste.' This principle has been applied by Haughton to twenty of the Vesuvian lavas, whose date of eruption ranges between 1631 and 1868. The lavas vary but slightly in composition. The following tables show the ultimate and proximate composition of two lavas separated by more than 200 years.

Ultimate analysis: a. Lava della Scala, 1631; b. Fosso Grande, 1858.

	SiO^2	P^2O^5	F	Cl	Al^2O^3	Fe^2O^3	FeO	MnO	TiO	CaO	MgO	K^2O	Na^2O	H^2O
a.	47.47	0.45	0.08	0.39	16.67	4.20	5.90	1.15	0.23	9.98	4.34	7.46	2.28	0.08
b.	46.36	—*	0.06	—*	18.60	4.12	4.94	1.00	0.29	9.09	4.00	7.18	2.96	0.40

* Not determined.

The proximate constitution of the same lavas, determined by the method of indeterminate analysis, and Haughton's principle above alluded to, is:

	Leucite	Anorthite	Magnetite	Olivine	Augite	Nephelite	Sodalite	Apatite	Paste
a.	40.6	6.9	4.9	traces	31.1	6.5	trace	1.1	8.9
b.	40.8	12.3	4.8	trace	28.6	—	7.1	—	6.34

The paste of 1631 contained 37.2 per cent. SiO_2 , 16.1 CaO, and 46.7 FeO, and may therefore be represented by the formula $\text{CaO}, \text{FeO}, \text{SiO}_2$.

Nodules in the Lava of Santorin, Grecian Archipelago.—According to Fouqué (*Compt. rend.* lxxx. 631), some of these nodules are hollow, while others are completely filled. The hollow nodules contain wollastonite, together with fassaite, less frequently with melanite; they also contain several undetermined minerals, including a chlorinated calcio-sodic silicate. In the perfectly filled nodules melanite is wanting, but quartz is said to occur. The nodules are traversed by greyish veins of lava, in which a vitreous ground-mass predominates. The following are analyses of these bodies:

Wollastonite.					
	Very pure	Cracked, with Enclosures	Associated with Fassaite		Associated with Garnet (Melanite)
Silica	46.2	45.5	43.9	45.7	45.0
Lime	41.8	43.0	41.3	42.2	42.1
Magnesia	1.5	0.8	2.0	1.9	1.6
Alumina	7.1	7.2	9.5	8.6	8.1
Sesquioxide of iron	2.9	2.8	2.5	2.5	2.8
	99.5	99.3	99.2	100.0	99.6
Melanite Garnet Fassaite Pyroxene					
Silica		35.6		46.8	
Alumina		12.2		10.1	
Sesquioxide of iron		16.8		10.4	
Lime		33.3		24.9	
Magnesia		1.2		6.8	
		99.1		99.0	

Fouqué has also analysed masses rich in oligoclase, which are enclosed in the Santorin lavas. These masses, which to the naked eye appear compact, are resolved by microscopic examination into aggregates of predominant felspar, less abundant pyroxene, and a small proportion of magnetic iron oxide, all irregularly imbedded in a greenish-brown vitreous mass. The majority of the pyroxene crystals are found, on closer optical examination, to be rhombic, and have been recognised by Des Cloizeaux as *hypersthene*; the minority are monoclinic, and consist of true *augites*. Analyses: (1) Oligoclase; (2) Hypersthene; (3) the entire aggregates.

	SiO_2	$\text{Fe}^{\text{O}}\text{O}_3$	$\text{Al}^{\text{O}}\text{O}_3$	CaO	MgO	Na^{O}	K^{O}	Sp. gr.
1.	59.7	0.4	23.2	7.9	1.0	6.6	0.8 =	99.6 2.629
2.	48.6	21.3	6.0	3.2	20.0	trace	— =	99.1 3.472
3.	58.4	8.1	20.7	6.0	2.7	3.7	0.5 =	100.3 2.687

The species of felspar recognised by Fouqué in the latest eruption of Santorin are albite, oligoclase, labradorite, and anorthite.

On the volcanic phenomena of Santorin, see further '*Santorin et ses Éruptions*,' par F. Fouqué, 4to. Paris, 1879; abstr. *Jahrbuch für Mineralogie*, 1880; ii. *Band. Referate*, 305-309; *Chem. Soc. J.*, July 1881.

II. LIQUID VOLCANIC PRODUCTS.

Water is the liquid which most frequently makes its appearance in all manifestations of volcanic activity. Indeed, it is frequently asserted that volcanic phenomena depend upon the presence of water, and that superheated steam is the cause of all the phenomena of ejection which volcanoes present. Steam is sometimes continuously emitted for years from the craters of volcanoes, or from fissures or orifices on their flanks, or from the floors of otherwise dormant craters. 'That the lava of volcanoes,' says Professor Judd, 'is a fluid mass containing imprisoned water, which, as it is relieved from pressure, flashes into steam, is now recognised by all geologists.' The changes of composition produced by the action of superheated water upon rocks are very various. These changes can be very advantageously studied in Iceland, and Bunsen has done much to extend our knowledge of thermal springs and water-metamorphism in that country. The springs of Iceland are distinguished from all other

European thermal springs by the large quantity of silica which they contain. They are either acid or alkaline. The former are connected with the solfataras, or *namars*, and owe their acidity to the presence of ammonia, soda, or potash alums. They contain various sulphates and chlorides, and deposit sulphur and gypsum. The alkaline springs are the commoner of the two, and constitute *Geysirs*, *Laugs*, and *Hvers*. Their alkaline reaction is due to the presence of alkaline sulphides and carbonates, which serve as solvents for the silica, and produce deposits of siliceous sinter or *geyserite*.

The following is an analysis by Bunsen of a slightly acid water taken in August 1846 from one of the largest of the mud cauldrons of the Reykjahlid solfataras, between the N.E. declivity of the Namarfjall and the Burfell lava stream, in 10,000 parts:

CaSO ⁴	MgSO ⁴	(NH ⁴) ² SO ⁴	Al ³ (SO ⁴) ³	Na ² SO ⁴	K ² SO ⁴	SiO ²	Al ² O ³	H ² S
1.2712	1.0662	0.7333	0.3261	0.2674	0.1363	0.4171	0.0537	0.0820

The water of the Great Geysir, analysed in Bunsen's laboratory by Dr. Sandberger in 1846, gave in 10,000 parts:

SiO ²	Na ² CO ³	(NH ⁴) ² CO ³	Na ² SO ⁴	K ² SO ⁴	MgSO ⁴	NaCl	Na ² S	CO ²
0.5097	0.1939	0.0083	0.1070	0.0475	0.0042	0.2521	0.0088	0.0577

None of the rocks of Iceland resist the decomposing action of thermal waters, and these decompositions may be traced in the rocks of all ages. A variety of products is the result. The siliceous compounds with which these waters come into contact are formed into acid or basic silicates; the former are dissolved by the waters, the latter give rise to insoluble strata of clay.

Mud.—Certain small volcanic vents in various parts of the world bring to the surface quantities of hot argillaceous mud, resulting from the action of water containing various substances in solution, upon different kinds of rock, at varying temperatures and pressures.

Sulphuric acid is often found in the neighbourhood of volcanoes, containing in solution various sulphates, which it has dissolved out of the different rocks with which it has been in contact. It is found in cavities in the small volcanic mountain called Zoccolino, near Siena; in the stream issuing from Mount Purace, between Quito and Bogoto; in a stream proceeding from Mount Idienne, in Java; and elsewhere. The water of the Rio Vinagre, which rises near the Volcano Purace, has been found by Boussingault to contain in 100,000 parts:

SO ²	HCl	SiO ²	Al ³ O ³	CaO	Na ² O
134.75	121.70	2.37	40.28	13.33	12.32 = 324.75

A torrent near Pasto was sufficiently acid to evolve hydrogen in contact with zinc. Near the Rio Guali a thermal spring was met with which contained 634.6 parts of sulphuric acid in 100,000. The sulphuric acid is undoubtedly produced by the action of hydrochloric acid at a temperature of from 700° to 900° upon sulphates; and the hydrochloric acid results from the action of aqueous vapour and silica upon chlorides at a red heat (*Compt. rend.* 78, p. 455 *et seq.*; *Chem. Soc. J.* 1874, p. 562).

Liquid Hydrocarbons.—Various liquid hydrocarbons have been found from time to time in the neighbourhood of volcanoes, as by Breislak at the foot of Vesuvius, in the Val di Noto in Sicily, and among the extinct volcanoes of Auvergne. Quite recently Silvestri has detected a mineral oil in the cavities of a prehistoric doleritic lava found near Paternò, on the flanks of Etna (see PARAFFINS, p. 1489). It was found in close proximity to the clay deposits of a mud volcano. The lava consisted mainly of augite with crystals of olivine and labradorite. It contained numerous cavities lined with arragonite and filled with a mineral oil, which latter was found to constitute about 1 per cent. of the whole weight of the lava. The mineral oil was taken from the lava at a temp. of 24° C., and it solidified at 17° to a yellowish-green mass, which on analysis gave the following composition: *

Liquid hydrocarbons boiling at 79°	= 17.97
Hydrocarbons solidifying below 0°, and boiling between 280° and 400°	= 31.95
Paraffin melting between 52° and 57°	= 42.79
Asphalt containing 12 per cent. of ash	= 2.90
Sulphur	= 4.32

99.93

III. GASEOUS VOLCANIC PRODUCTS.

The principal gaseous products of volcanoes are oxygen, hydrogen, nitrogen, chlorine, steam, hydrochloric acid, ammonia, sulphurous acid, hydrogen sulphide, carbonic acid, and marsh gas. The gases which are evolved from the principal vent after the issue of lava frequently consist of little else than atmospheric air. Hydrochloric acid and sulphurous acid, particularly the former, are products of intense volcanic activity. Carbonic acid and nitrogen appear during the more languid periods of activity, while hydrogen sulphide holds an intermediate position, and is never evolved during the most active stage.

The following analysis by Bunsen of the gases of a fumerole in the great crater of Hekla, in 1845, will illustrate the general nature of the gases evolved after the emission of lava:

N	O	CO ²	SO ²
81.81	14.21	2.44	1.54 = 100

At the solfatara of Krisuvik, in Iceland, jets of steam mixed with other gases issue from the ground with sufficient force to project stones as large as the fist to a height of several feet. The jets of vapour were found by Bunsen to contain in 100 parts: 62.30 H²O, 15.47 CO², 1.17 H²S, 0.76 H, and 0.30 N. The mixed gases separated from the aqueous vapour contained in 100 parts: 87.43 CO², 6.60 H²S, 4.30 H, and 1.67 N.

In the course of twenty-four hours, this fumerole yields approximately 223 cubic meters of hydrogen sulphide and 12 cubic meters of hydrogen. A neighbouring fumerole gave a mixture of gases containing 15.71 per cent. of sulphuretted hydrogen.

The following is the analysis by Bunsen of a fumerole gas from Reykjahlidh, in the north of Iceland, remarkable for the large amount of hydrogen which it contains:

CO ²	H	H ² S	N
30.00	25.13	24.13	0.72* = 100

Fumerole gas from the immediate neighbourhood of the great geysir at Haukadalur gave:

N	CO ²	H	H ² S
84.11	8.92	6.59	0.38 = 100

Silvestri analysed some of the fumerole gases of the eruption of Etna in 1865, and found them to consist of:

CO ²	H ² S	O	N
50.5	11.9	7.0	30.5

The gas evolved from a fumerole in the volcanic island of Santorin after the eruption of 1866 was found by Gorceix (*Compt. rend.* lxxv. 270) in 1870 to contain 19.4 HCl, 12.0 SO², and 68.5 CO². Gorceix has also analysed the gases emitted from the fumeroles of Nisyros (*Compt. rend.* lxxviii. 444-6). Fumerole No. 1 was situated within the aperture formed in June 1873; No. 2, on the lateral wall; Nos. 3-6 were on the flanks of the original crater. The carbonic acid and sulphuretted hydrogen obviously decrease with the increase of distance from the centre of activity.

	Temperatures 100°	100°	96°	92°	70°	55°
	I	II	III	IV	V	VI
Sulphuretted hydrogen	48.8	44.5	4.6	1.5	—	—
Carbonic acid	40.9	49.2	1.8	14.7	7.0	5.5
Oxygen	1.1	1.0	13.8	15.6	18.1	18.2
Nitrogen	3.2	5.2	63.5	67.8	74.8	79.2

Of the various gaseous volcanic products *free hydrogen* is at first sight the most difficult to account for. Bunsen has shown that the conversion of pyroxenic rocks into palagonite is accompanied by a considerable disengagement of pure hydrogen, which results from the oxidation of ferrous silicate into ferric silicate. This change, however, presupposes so high a temperature that carbonic acid could not exist in contact with hydrogen without suffering partial reduction to carbonic oxide; but no trace of this gas is found in volcanic emanations. The formation of hydrogen and the other fumerole gases may, however, be supposed to take place as follows. When sulphur-vapour and steam come into contact with pyroxenic rocks at a red heat, a partial decomposition of ferric oxide takes place, and the sulphur is divided between the iron and the oxygen, forming sulphurous acid and sulphide of iron, FeS². If steam now comes into contact with the sulphide at a red heat, hydrogen sulphide is formed together with magnetic iron oxide, FeO⁴. If the temperature slightly exceeds a red heat, a part of the hydrogen sulphide is decomposed into hydrogen and sulphur. Bunsen found that when basalt is heated to redness in hydrogen sulphide, and after-

* So in the original paper; probably a misprint for 20.72.

wards raised to a higher temperature in a current of steam, a gaseous mixture is evolved, giving by analysis 93.99 per cent. H_2S and 6.01 H. This reaction explains the occurrence of hydrogen in fumarole gases. Bunsen considers that the metallic copper found in the palagonite tuff of the Faroe Islands has been reduced by hydrogen from copper chloride.

Diego Franco (*Ann. Chim. Phys.* [4], xxx. 87; *Jahresb. f. Chem.* 1873, 1229) has demonstrated the emission of carbon dioxide in all stages of volcanic action, especially from Vesuvius, in which he has found this gas both in the central cone and in the flowing lavas. He has also given numerous analyses of gases emitted from flowing and from hardened lava, and found carbon dioxide in them all.

G. F. R.

VOLUME, SPECIFIC. *Atomic Volume.*—(1). **Of Liquids.** By dividing the specific gravities of liquids taken at the temperatures at which their vapour-tensions are equal to the standard atmospheric pressure—that is, at their ordinary boiling points—into their molecular weights, certain comparable values are obtained which are known as specific volumes. If the specific gravities are referred to water at 4°C ., these values represent the number of cubic centimeters occupied by the relative molecular weights of liquids, expressed in grams, at their respective boiling points under the standard pressure. The numbers so obtained were first shown by Kopp to exhibit certain definite relations which may be briefly indicated as follows:

1. *In many instances differences in specific volume are proportional to differences in corresponding chemical formulae.* Thus a difference of CH_2 in a homologous series corresponds to a difference of about 22 in the specific volume, or $(\text{CH}_2)x = 22x$. On comparing the specific volumes of similarly constituted haloid compounds, it is seen that the substitution of n atoms of bromine for an equal number of chlorine atoms increases the specific volume by $5n$.

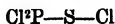
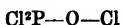
2. Isomeric and metameric liquids have, as a rule, the same specific volume.

3. The substitution of an atom of carbon for 2 of hydrogen makes no alteration in the specific volume of members of certain groups of organic liquids.

It would seem to follow, from Kopp's observations, that the specific volume of a liquid formed by the union of two other liquids is equal to the sum of the specific volumes of its components. It may also be inferred that the members of the same family of elements possess identical specific volumes; thus the common value of phosphorus, arsenic, and antimony would appear to be about 27; that of silicon, titanium, and tin would seem to be about 35.

On the basis of these conclusions Kopp was able to calculate certain fundamental values for the specific volumes of the elements in combination. These values are as a rule constant for the particular element; thus carbon has invariably the value 11, hydrogen that of 5.5. Exceptions are observed in the case of the chemical analogues oxygen and sulphur. Each of these bodies has two values, depending, it would seem, on its mode of combination, or on its relation to the remaining atoms in the molecule. For example, acetone and allyl alcohol have each the empirical formula $\text{C}_3\text{H}_6\text{O}$, but the specific volume of acetone is 78.2, whilst that of allyl alcohol is 73.8. The constitution of acetone may be expressed by the formula $\text{CH}_3\text{CO}\cdot\text{CH}_3$, whilst that of allyl alcohol is $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$. In the case of acetone the affinities of the oxygen are wholly satisfied by the carbon—that is, we have reason to think that the oxygen-atom is more intimately associated with one of the carbon atoms than it is with any one of those of the other elements, whereas in allyl alcohol a moiety of the combining value would seem to be satisfied by carbon and the remainder by hydrogen. It appears, then, that when oxygen is united to an element by both its affinities, its specific volume is 12.2; when it is attached by only one combining unit, its specific volume is 7.8. The corresponding values for sulphur are 28.6 and 22.6.

Thorpe has pointed out (*Proc. Roy. Soc. Ed.* 1875) that these differences in the values for the specific volumes of oxygen and sulphur may be employed to throw light upon the constitution of such bodies as phosphoryl trichloride and thiophosphoryl trichloride. If the phosphorus in these substances be regarded as trivalent, they must possess the constitution



If, on the other hand, the phosphorus is quinquivalent, they must be written



It is obvious that the knowledge of the specific volumes of PCl_3 , POCl_3 , and PSCl_3 will serve to indicate the mode of combination of the oxygen and sulphur, and hence to determine the atomic value of the phosphorus in these compounds, provided that

the specific volume of the phosphorus is invariable, or is independent of its atomic value.

The sp. vol. of PCl_3 , according to Thorpe, is 93.3; Pierre found 93.5; Buff, 93.3; the mean of these numbers is 93.4. Buff and Thorpe found the sp. vol. of POCl_3 101.4; whilst that of PSCl_3 , according to Thorpe, is 116.1.

Sp. vol. of PCl_3	—	Sp. vol. PCl_3	=	Sp. vol. of O	Calc. sp. vol.
101.4	—	93.4	=	8.0	7.8
Sp. vol. PSCl_3	—	Sp. vol. PCl_3	=	Sp. vol. of S	
116.1	—	93.4	=	22.7	22.6

That this close agreement between the observed and calculated values is not a mere coincidence is seen from the fact of the difference between the two values respectively of oxygen and of sulphur; in the one case the difference is 4.4, in the other it is 6.0.

The observations of Pisati and De Franchis (*Gazz. Chim. ital.* 1874; *Ber. deutsch Chem. Ges.* 1875, 70; *Jahr.* 1875, 50) of the thermal expansion of solid and liquid phosphorus afford a determination of the specific volume of this element in the free state. The phosphorus melted at 44.4° , and boiled at 278.3° under a pressure of 762 mm. The following numbers, selected from the numerous observations of Pisati and De Franchis, show its specific gravity at various temperatures:

	Solid		Liquid
0°	1.83676	40°	1.74924
20°	1.82321	100°	1.69490
44°	1.80681	200°	1.60270
		280°	1.52867

The ratio of the volumes of solid and liquid phosphorus at 40° was 1.03446, and at 44° 1.0504. Kopp found 1.0343 at 44° . The volume of the solid phosphorus at t° referred to that at 0° is expressed by

$$V_t = V_0 + 0.000200t + 0.000000115t^2.$$

The expansion of liquid phosphorus between 50° and 280° is given by the expression

$$V_t = V_{50} + 0.0002369(t - 50) + 0.0000002115(t - 50)^2.$$

Pisati and De Franchis found some difficulty in preventing a partial transformation of the yellow phosphorus into the red modification, and the numbers denoting the specific gravity at higher temperatures are probably slightly too high on this account. The observation of Schrötter that melted phosphorus at 44° has a higher specific gravity (1.88) than when solid at 10° (1.83) was probably owing to the same cause. The specific volume of phosphorus calculated from the observations of Pisati and De Franchis is 20.2. A similar result has recently been obtained by Masson and Ramsay, who found the specific gravity of phosphorus at its boiling point to be 1.485, whence the specific volume = 20.91. The sp. vol. of phosphorus in the free state is therefore different from that which it possesses in such compounds as PCl_3 , PBr_3 , and $\text{PCl}_3\text{CH}_3\text{O}$. Whether it is different from that of the element as existing in POCl_3 , POBrCl_2 , and PSCl_3 depends upon the view which is taken of the constitution of these bodies; but there is no *a priori* reason for supposing that the volume of the combined phosphorus would be different in the two series of compounds. It may be contended, from the well-known anomaly in the vapour-density of the element, that free phosphorus and combined phosphorus are not in comparable molecular states.

The specific volume of nitrogen also appears to be variable. According to Kopp in the amines it is 2.3; in cyanogen and certain nitro-compounds it is about 17. No rational explanation of this difference has yet been given. In fact, the observations of Ramsay (*infra*) seem to afford widely different values for the specific volume of nitrogen in different amines, and appear also to show that this element has a distinct value in the pyridine series of bases. On the supposition that the atomic value of an element is variable, Buff has suggested (*Ann. Chem. Pharm.* Suppl. iv. 129) that its specific volume is a function of that value. So far as we know there is no *a priori* reason why oxygen, sulphur, and nitrogen should alone possess variable specific volumes. (Compare i. 440-452 and vi. 235-237.)

Thorpe has recently determined the sp. vol. of a large number of specially selected liquid substances (*Chem. Soc. J.* 1880, xxxvii. 145-394), with the view of obtaining facts for a discussion of the following points:

1. Is it definitely established that an element in combination has, as a rule, an invariable specific volume? May not the volume be modified by the number of the atoms of that particular element in the molecule? Is it altogether independent of the

general complexity of the molecule, or may not the specific volume of the molecule be a function of its weight?

2. Do the various members of a given family of elements possess identical specific volumes, or may not the volume be a function of the atomic weight?

3. Would a re-examination of the cases of so-called variable atomic value serve to show that the specific volume of an element is a function of that value, as Buff supposes?

4. The hypotheses of Mendelejeff and Meyer indicate the need for additional and more exact determinations of the values for the specific volumes of the elementary bodies.

The method of observation was essentially that employed by Kopp, which involves the determination of the sp. gr., boiling point, and rate of thermal expansion of the liquid. For the details of the modes of experiment, which differed in many respects from those hitherto adopted, we must refer to the original memoir (*loc. cit.*) The sp. grs. were taken at 0°, and are compared with water at 4°; the boiling points are corrected and reduced to the standard pressure, and the rates of expansion are represented by expressions of the form

$$V = 1 + at + bt^2 + ct^3.$$

All temperatures are expressed in air-thermometer degrees.

The results are contained in the following tables. Table I, gives the several values of the coefficients in the expression representing the thermal expansion of the particular liquids investigated.

Table II. shows the relative volumes of the several liquids at every 10° between 0° and their boiling points.

Table III. shows the formulæ and molecular weights of these bodies, their boiling points under the standard pressure, their relative volumes at this temperature, their specific gravities at 0°, and at their respective boiling points, and lastly their specific volumes.

The conclusions which Thorpe deduces from his observations may be stated as follows.

1. It does not seem absolutely proved that isomeric liquids of the same chemical type, using that phrase in the sense in which Kopp employs it, have invariably the same specific volume. It is certain, for example, that ethylidene chloride and Dutch liquid have not the same specific gravity at their boiling points, and accordingly have not the same specific volume. The observations have given for—

	Sp. gr. at b.p.	Sp. vol.
Ethylene chloride . . .	1.15635	85.34
Ethylidene chloride . . .	1.10923	88.96
		3.62

This difference of 3.62 cannot be attributed to errors of observation. Moreover the specific volumes of ethylene chloride and of its analogues, $C^2H^1Br^2$ and $C^2H^1Cl^1$, are considerably below the numbers calculated by means of Kopp's values.

	Observed	Calculated	Diff.
Ethylene chloride . . .	85.3	89.5	4.2
„ bromide . . .	97.1	99.5	2.4
„ chloriodide . . .	101.0	104.2	3.2

It seems not improbable that the specific volume of carbon or of hydrogen, or of both, may be slightly modified by the mode in which the atoms are grouped in a compound; that we may have, in fact, variations of a kind analogous to that which Gladstone, and more recently Brühl, have shown to exist in the atomic refraction of carbon, dependent on the manner of its combination. Indeed, it is not improbable that an intimate connection exists between the refractive power of such compounds and their specific volumes. Landolt has inferred that differences of molecular grouping in no way affect the refractive index of the constituent atoms, and Gladstone has shown that as a general law the molecular refractive power of a body is equal to the sum of the refraction of the atoms, just as it has been inferred that the specific volume of carbon is invariable, and that the specific volume of a compound liquid is equal to the sum of the specific volumes of its constituent elements or compound radicles. Exceptions, however, are known to this law. Thus the molecular refraction of many benzene derivatives, ethereal oils, and terpenes, and other bodies relatively rich in carbon, is considerably greater than that calculated from their atomic refractions. Brühl has succeeded in detecting the relation between the constitution of these bodies and their optical character; he has shown that their refractive power depends upon the mode of combination of the constituent atoms. It appears, for example, that in the

case of unsaturated bodies the atoms, which are more than once directly united to each other, exert a greater influence in propagating light than atoms which with the same atomic value are united to other atoms. Gladstone has pointed out that isomeric bodies occasionally differ widely in their optical properties. Thus aniline and picoline, each C^8H^7N , have widely different refraction equivalents. It is also certain that they have totally distinct specific volumes; thus:

Aniline
106.2

Picoline
111.5

It may be further noted that a large number of these bodies, of which the molecular refraction is greater than the computed value, have also a specific volume considerably

TABLE I.

Substance	a	b	c
Bromine	0.00106218	0.00000187714	-0.000000003085
Iodine monochloride . .	0.00091590	0.00000083296	0.000000002750
Ethylene bromide . . .	0.00095285	0.00000068346	0.000000003947
Ethylene chloriodide . .	0.00093692	0.00000041513	0.000000004501
Ethylene chloride . . .	0.00115303	0.00000082569	0.000000009625
Ethidene chloride . . .	0.00128402	0.00000189062	0.000000007848
Acetyl chloride	0.00136948	0.00000207390	0.000000012185
Trichloracetyl chloride .	0.00109113	0.00000027205	0.000000008293
Chloral	0.00108715	0.00000280306	-0.000000016040
Pentachlorethane . . .	0.00094901	-0.00000007450	0.000000005280
Methene chloride . . .	0.00130805	0.00000273596	-0.000000001330
Chloroform	0.00123024	0.00000171380	0.000000008338
Chloropierin	0.00110070	0.00000045676	0.000000007833
Carbon tetrachloride . .	0.00120719	0.00000067109	0.000000013478
Bromoform	0.00094116	0.00000027800	0.000000004260
Trichlorobromomethane .	0.00108231	0.00000065582	0.000000005858
Propionitrile	0.00122775	0.00000204064	0.000000003675
Epichlorhydrin	0.00102660	0.00000061974	0.000000006657
Allyl alcohol	0.00099371	0.00000059986	0.000000012285
Acetone	0.00135293	0.00000302426	-0.000000000290
Heptane	0.00121023	0.00000111330	0.000000011740
Ethyl-amyl	0.00123940	0.00000119318	0.000000013060
Octane	0.00118304	0.00000018665	0.000000012947
Di-isobutyl	0.00119701	0.00000062122	0.000000014166
Aniline	0.00086295	0.00000027351	0.000000003466
Picoline	0.00096653	0.00000084590	0.000000004567
Nitrogen tetroxide . . .	0.001591	-0.00000397015	0.00000002153
Silicon tetrachloride . .	0.00133095	0.00000280978	0.000000002157
Titanium tetrachloride .	0.00098261	0.00000050553	0.000000005131
Tin tetrachloride . . .	0.00116055	0.00000064617	0.000000007727
Phosphorus trichloride .	0.00115920	0.00000116370	0.000000008029
Phosphorus tribromide .	0.00084117	0.00000054289	0.000000001889
Phosphoryl chloride . .	0.00107510	0.00000099131	0.000000005757
Thiophosphoryl chloride .	0.00100850	0.00000065582	0.000000004746
Phosphoryl bromo- chloride	0.00100520	0.00000049053	0.000000004407
Ethoxyphosphorus chloride	0.00102304	0.00000187367	-0.000000000610
Phenacyl chloride . . .	0.00082582	0.00000014461	0.000000002863
Vanadyl trichloride . .	0.00096524	0.00000089826	0.000000003192
Arsenic trifluoride . . .	0.001443	0.000000297	—
Arsenic trichloride . . .	0.00099134	0.00000084914	0.000000002755
Thionyl dichloride . . .	0.00116419	0.00000091418	0.000000009537
Sulphothionyl chloride .	0.00093425	0.00000041082	0.000000004077
Chlorosulphonic acid . .	0.00090505	0.00000011865	0.000000002394
Sulphuryl dichloride . .	0.00123065	0.00000075938	0.000000014587
Disulphuryl chloride . .	0.00096830	0.00000086710	0.000000001862
Chromyl dichloride . . .	0.00095860	0.00000010737	0.000000001962
Carbon disulphide . . .	0.00115056	0.00000111621	0.000000017476

TABLE II.

ΔC	Bromine, Br	Iodine monochloride, ICl	Ethylene bromide, $C^2H^4Br^2$	Ethylene chloriodide, C^2H^4Cl	Ethylene chloride, $C^2H^4Cl^2$	Ethylene chloride, $C^2H^4Cl^2$	Acetyl chloride, C^2H^3OCl	Trichloroacetyl chloride, C^2Cl^3
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101081	100925	100960	100942	101162	101304	101391	101095
20	102197	101867	101936	101894	102347	102650	102832	102200
30	103347	102830	102931	102860	103559	104044	104328	103320
40	104592	103815	103946	103843	104806	105489	105888	104461
50	105742	104822	104984	104845	106092	106991	107518	105627
60	106983	105855	106049	105868	107423	108554	—	106824
70	—	106914	107140	106916	108806	—	—	108066
80	—	108001	108262	107992	110246	—	—	109328
90	—	109118	109417	109097	—	—	—	110645
100	—	110267	110607	110234	—	—	—	112013
110	—	—	111834	111408	—	—	—	113436
120	—	—	113101	112619	—	—	—	114918
130	—	—	114409	113871	—	—	—	—
140	—	—	—	115166	—	—	—	—

ΔC	Chloral, C^2Cl^3OH	Pentachloroethane, C^5HCl^5	Methene chloride, CH^2Cl^2	Chloroform, $CHCl^3$	Chloropierin, $C(NO^2)^2Cl^2$	Carbon tetrachloride, CCl^4	Bromoform, $CHBr^3$	Trichlorobromethane, CCl^3Br
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101114	100949	101335	101248	101106	101215	100944	101089
20	102274	101899	102724	102536	102226	102452	101897	102196
30	103470	102855	104167	103867	103365	103718	102868	103322
40	104694	103818	105662	105248	104528	105022	103837	104472
50	105936	104792	—	106684	105718	106372	104829	105649
60	107186	105781	—	108179	106941	107776	105839	106857
70	—	106788	—	—	108202	109241	106870	108098
80	—	107815	—	—	109505	110777	107925	109378
90	—	108866	—	—	110855	—	109006	110699
100	—	109944	—	—	112256	—	110116	12065
110	—	111052	—	—	113714	—	111256	—
120	—	112193	—	—	—	—	112430	—
130	—	113371	—	—	—	—	113641	—
140	—	114587	—	—	—	—	114890	—
150	—	115849	—	—	—	—	116180	—
160	—	117156	—	—	—	—	—	—

TABLE II.—continued.

ΔC	Propionitrile, C^3H^5CN	Epichlorhydrin, C^3H^5OCl	Allyl alcohol, C^3H^5OH	Acetone, C^3H^6O	Heptane, C^7H^{16}	Ethyl-amyI, C^7H^{16}	Octane, C^8H^{18}	Di-isobutyl, C^8H^{18}
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101249	101033	101026	101383	101222	101253	101186	101205
20	102541	102083	102072	102827	102474	102537	102384	102430
30	103879	103154	103145	104330	103763	103861	103601	103685
40	105267	104248	104252	105894	105094	105232	104845	104978
50	106707	105371	105402	107517	106476	106659	106124	106317
60	108202	106526	106601	109209	107916	108148	107445	107712
70	109755	107718	107857	—	109420	109709	108817	109169
80	111367	108950	109176	—	110995	111348	110247	110699
90	113044	110227	110568	—	112650	113070	111742	112309
100	114786	111551	112038	—	114390	—	113312	114008
110	—	112929	—	—	—	—	114963	115804
120	—	114362	—	—	—	—	116702	—

ΔC	Aniline, C^6H^7N	Picoline, C^6H^7N	Nitrogen tetroxide, N^2O^4	Silicon tetrachloride, $SiCl^4$	Titanium tetrachloride, $TiCl^4$	Tin tetrachloride, $SnCl^4$	Phosphorus trichloride, PCl^3	Phosphorus tribromide, PBr^3
0	100000	100000	100000	100000	100000	100000	100000	100000
10	100866	100975	101573	101359	100988	101168	101172	100847
20	101740	101971	103196	102776	101990	102353	102371	101706
30	102623	102986	—	104252	103007	103561	103604	102577
40	103518	104031	—	105787	104044	104795	104874	103463
50	104426	105101	—	107384	105104	106061	106187	104365
60	105351	106202	—	109044	106188	107363	107547	105283
70	106294	107337	—	—	107302	108706	108960	106218
80	107256	108507	—	—	108447	110094	110429	107173
90	108241	109717	—	—	109627	111532	—	108148
100	109250	110963	—	—	110845	113024	—	109143
110	110285	112153	—	—	112103	114576	—	110161
120	111348	113606	—	—	113406	—	—	111202
130	112442	114998	—	—	114756	—	—	112266
140	113569	—	—	—	116155	—	—	113357
150	114729	—	—	—	—	—	—	114476
160	115927	—	—	—	—	—	—	115622
170	117163	—	—	—	—	—	—	116796
180	118441	—	—	—	—	—	—	—

● TABLE II.—continued.

ΔC	Phosphoryl chloride, POCl_3	Thiophosphoryl chloride, PSCl_3	Phosphoryl bromide, POBrCl	Ethoxyphosphorus chloride, $\text{PCl}_2\text{C}_2\text{H}_5\text{O}$	Phenylphenyl chloride, $\text{PCl}_2\text{C}_6\text{H}_5$	Vanadyl chloride, VOCl_3	Arsenic fluoride, AsF_3	Arsenic chloride, AsCl_3
0	100000	100000	100000	100000	100000	100000	10000	100000
10	101086	101025	101010	101042	100828	100975	10145	101000
20	102194	102047	102034	102121	101660	101969	10290	102019
30	103330	103097	103072	103237	102498	102985	10436	103058
40	104496	104169	104128	104388	103345	104025	10582	104119
50	105696	105266	105204	105576	104201	105091	10729	105203
60	106932	106390	106303	106800	105069	106184	10876	106313
70	108209	107544	107428	108058	105950	107306	—	107449
80	109530	108731	108581	109352	106846	108460	—	108615
90	110898	109953	109765	110681	107758	109647	—	109811
100	112318	111215	110983	112043	108689	110870	—	111038
110	113792	112519	112238	113439	109640	112129	—	112299
120	—	113966	113530	114869	110613	113428	—	113595
130	—	—	114864	—	111609	114767	—	114929
140	—	—	116243	—	112631	—	—	—
150	—	—	—	—	113679	—	—	—
160	—	—	—	—	114756	—	—	—
170	—	—	—	—	115863	—	—	—
180	—	—	—	—	117003	—	—	—
190	—	—	—	—	118176	—	—	—
200	—	—	—	—	119385	—	—	—
210	—	—	—	—	120632	—	—	—
220	—	—	—	—	121916	—	—	—
230	—	—	—	—	123242	—	—	—

ΔC	Thionyl chloride, SOCl_2	Sulphothionyl chloride, SSCl_2	Chlorosulphonic acid, SO_2HCl	Sulphuryl dichloride, SO_2Cl_2	Disulphuryl chloride, $\text{S}_2\text{O}_2\text{Cl}_2$	Chromyl dichloride, CrO_2Cl_2	Carbon bisulphide, CS_2
0	100000	100000	100000	100000	100000	100000	100000
10	101174	100939	100906	101240	100977	100969	101163
20	102373	101888	101817	102503	101973	101962	102360
30	103601	102851	102732	103800	102988	102978	103599
40	104864	103829	103655	105138	104024	104019	104892
50	106169	104825	104685	106526	105082	105086	106250
60	107520	105841	105525	107973	106162	106181	—
70	108924	106881	106476	109487	107267	107304	—
80	110387	107946	107439	—	108397	108457	—
90	—	109038	108416	—	109553	109640	—
100	—	110160	109409	—	110736	110856	—
110	—	111315	110418	—	111948	112105	—
120	—	112507	111445	—	113190	113388	—
130	—	113735	112492	—	114463	—	—
140	—	115003	113560	—	115767	—	—
150	—	—	114651	—	—	—	—
160	—	—	115765	—	—	—	—

TABLE III.

Substance	Formula	Mol. weight	B. p. Δ	Vol. at b. p.	Sp. gr. at 0°	Sp. gr. at b. p.	Sp. vol.
Bromine	Br^2	159.50	59.27	1.06911	3.18828	2.98218	53.48
Iodine monochloride	ICl	161.90	101.3	1.10419	3.18223	2.88196	56.18
Ethylene bromide	$\text{C}^2\text{H}^2\text{Br}^2$	187.44	131.45	1.24602	2.21324	1.93124	97.06
Ethylene chloriodide	$\text{C}^2\text{H}^2\text{ICl}$	189.84	140.1	1.15179	2.16439	1.87915	101.03
Ethylene chloride	$\text{CH}^2\text{Cl.CH}^2\text{Cl}$	98.68	83.5	1.10764	1.28082	1.15635	85.34
Ethidene chloride	CH^2CHCl^2	98.68	59.0	1.08538	1.20394	1.10923	88.96
Acetyl chloride	CH^3COCl	78.27	50.73	1.07640	1.13773	1.05698	74.05
Trichloroacetyl chloride	CCl^3COCl	181.38	118.0	1.14617	1.65640	1.44517	125.51
Chloral	CCl^3COH	147.01	97.2	1.11771	1.54480	1.3821	106.37
Pentachlorethane	$\text{CCl}^5\text{CHCl}^2$	201.79	159.1	1.17008	1.70893	1.46052	138.2
Methene chloride	CH^2Cl^2	84.71	41.6	1.05905	1.37776	1.30093	65.12
Chloroform	CHCl^3	119.08	61.2	1.08362	1.52657	1.40877	84.53
Chloropierin	$\text{C}(\text{NO}^2)\text{Cl}^3$	164.01	111.0	1.13999	1.69225	1.48444	110.49
Carbon tetrachloride	CCl^4	153.45	76.74	1.10268	1.63195	1.47999	103.68
Bromoform	CHBr^3	252.22	151.2	1.16338	2.83413	2.43611	103.53
Trichlorobrommethane	CBrCl^3	197.83	104.07	1.12634	2.05496	1.82446	108.43
Propionitrile	$\text{C}^2\text{H}^3\text{CN}$	54.92	97.08	1.14270	0.80101	0.70098	78.35
Epichlorhydrin	$\text{CH}^2\text{Cl.CH.O.CH}^2$	92.24	116.55	1.13861	1.20313	1.05667	87.29
Allyl alcohol	$\text{CH}^2\text{CH.CH}^2\text{OH}$	57.87	96.6	1.11529	0.86990	0.77998	74.10
Acetone	$\text{CH}^3\text{CO.CH}^3$	57.87	56.53	1.08600	0.81858	0.75369	76.78
Heptane	$\text{CH}^3(\text{CH}^2)^3\text{CH}^3$	99.79	98.43	1.14111	0.70048	0.61386	162.56
Ethyl-amil	$(\text{CH}^3)_2\text{CH}(\text{CH}^2)^2\text{CH}^3$	99.79	90.3	1.13126	0.69692	0.61606	161.98

Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	113.76	125.46	1.17693	0.71883	0.61077	186.26
Di-isobutyl	$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	113.76	108.53	1.15534	0.71110	0.61549	184.83
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	92.83	183.7	1.18924	1.03790	0.87274	106.37
Picoline	$\text{CH}_2=\text{C}=\text{CH}-\text{CH}=\text{N}$ $\text{CH}_2=\text{CH}-\text{CH}=\text{N}$	92.83	133.5	1.15497	0.96161	0.83258	111.50
Nitrogen tetroxide	N_2O_4	92.06	21.6	1.03523	1.4903	1.43058	63.95
Silicon tetrachloride	SiCl_4	169.48	57.57	1.08635	1.52408	1.40294	120.80
Titanium tetrachloride	TiCl_4	189.48	136.4	1.15647	1.76041	1.52223	124.47
Tin tetrachloride	SnCl_4	259.28	113.9	1.15197	2.27875	1.97813	131.07
Phosphorus trichloride	PCl_3	137.07	75.95	1.09827	1.61275	1.46845	93.34
Phosphorus tribromide	PBr_3	270.21	172.9	1.17140	2.92311	2.49541	108.28
Phosphoryl chloride	POCl_3	153.03	107.23	1.13378	1.71163	1.50967	101.37
Thiophosphoryl chloride	PSCl_3	169.05	125.12	1.14575	1.68820	1.45599	116.11
Phosphoryl bromochloride	POBrCl_2	197.41	137.6	1.15894	2.12065	1.83844	107.38
Ethoxyphosphorus chloride	$\text{PCl}_2\text{C}_2\text{H}_5\text{O}$	146.60	117.5	1.14509	1.30527	1.13989	128.61
Phenacyl chloride	$\text{PCl}_2\text{C}_6\text{H}_5$	178.52	224.6	1.2252	1.3428	1.10415	161.68
Vanadyl trichloride	VOCl_3	173.27	157.19	1.14387	1.85534	1.63073	108.25
Arsenic trifluoride	AsF_3	131.9	60.4	1.08824	2.6659	2.4497	53.84
Arsenic trichloride	AsCl_3	181.1	130.21	1.14956	2.20500	1.91813	94.37
Thionyl dichloride	SOCl_2	118.68	78.8	1.10208	1.67673	1.52143	78.01
Sulphothionyl chloride	SSCl_2	134.70	138.12	1.14571	1.70941	1.49201	90.28
Chlorosulphonic acid	$\text{SO}_2\text{O.HCl}$	116.23	155.8	1.15238	1.78474	1.54874	75.05
Sulphuryl dichloride	SO_2Cl_2	134.64	69.95	1.09479	1.70814	1.56025	86.29
Disulphuryl chloride	$\text{S}_2\text{O}_2\text{Cl}_2$	214.50	139.59	1.15713	1.85846	1.60610	133.55
Chromyl dichloride	CrO_2Cl_2	155.06	115.9	1.11560	1.96101	1.75780	88.21
Carbon disulphide	CS_2	75.93	46.04	1.05704	1.29215	1.22242	62.11

less than the calculated numbers. The specific gravity, boiling point, and rate of thermal expansion of benzene are known with great accuracy from the experiments of Kopp (i. 542), Louguinine (*Jahres.* vi. 260, 1867, 48), Pisati and Paternò, and Adrieenz (viii. 159).

Their observations afford the following values for the specific volume of benzene :

Kopp 95·94	Louguinine 95·08	Pisati & Paternò 95·94	Adrieenz 95·90	Mean 95·94
Calculated sp. vol.			99·0	

The observed values are extremely concordant, but they differ by more than 3 per cent. from the computed value. Differences of the same order are exhibited by a number of aromatic compounds.

Specific Volume.

	Observed (Kopp)	Computed	Diff.
Phenol	103·6	106·8	3·2
Benzyl alcohol	123·7	128·8	5·1
Benzoic acid	126·9	130·0	3·1
Benzoic aldehyde	118·4	122·2	3·8
Cymene	183·5	187·0	3·5
Napthalene	149·2	154·0	4·8

Our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene (and the derivatives in which the benzene group functions) would in all probability be different from that deduced from observations made for the most part on compounds of totally different constitution. Kopp (*Liebig's Annalen*, Supp. vi. 303) has shown, from Louguinine's observations, that whilst benzene has an abnormally low specific volume, its homologues show the constant increase of 22 in the volume for an increment of CH_2 , which is what might be anticipated, since these bodies are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group. Other values have, indeed, been calculated for carbon and hydrogen. Lothar Meyer makes $\text{H}=3$, and Loschmidt $\text{C}=14$ and $\text{H}=3\cdot5$; and, by assuming that half the carbon-atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value $3\cdot5$, we obtain a value for this hydrocarbon which is identical with the observed number.

2. The observations furnish additional evidence in support of the assumption already regarded by Kopp and others as highly probable, that an element or a compound radicle occupies the same volume in combination as in the free state. Direct observation shows that the sp. vol. of nitrogen tetroxide is 64: hence $\text{NO}^2=32$. The sp. vol. of chloroform is 84·5; that of chloropierin is 110·5. Chloropierin may be regarded as derived from chloroform by the replacement of an atom of hydrogen by an equivalent amount of NO^2 .

Sp. vol. of $\text{C}(\text{NO}^2)\text{Cl}^3$	110·5
CHCl^3	84·5
	<hr/>
Add sp. vol. of H	26·0
	5·5
	<hr/>
Calculated vol. of NO^2	31·5
Observed	32·0

Similar evidence is afforded by ethylene bromide, ethylene chloriodide, and propionitril.

Thorpe further concludes that there is at present no evidence in support of the hypothesis that the specific volume of an element in combination is modified by any possible variation in the affinity value which it may possess. It may turn out that the particular value to be assigned to carbon, for example, in the aromatic compounds is slightly different from that which it is found to possess in the fatty acids, or the corresponding alcohols and ethers, but there is no question as to the quantivalence of the carbon in these several groups of compounds. It is not, however, clearly established that any element, with the exception of oxygen, sulphur, and nitrogen, has a variable specific volume in combination. Hence the specific volume is altogether independent of the general complexity of the molecule, inasmuch as it is not modified by the number of the atoms of the particular element, in the molecule. Lastly, it is proved that the different members of a family of elements do not possess identical specific volumes; the volumes of the elements are periodic functions of their atomic weights. The values deduced by Thorpe from a discussion of his observations,

together with those of previous investigators, are contained in the following table. It also shows the relation of the specific volume to the atomic weight.

Atomic Weights.

I	II	III	IV	V	VI
H = 1	C = 11.97	Si = 28.0	Ti = 48		Sn = 117.8
	N = 14.01	P = 30.96	V = 51.2	As = 74.9	Sb = 120.0
	O = 15.96	S = 31.98	Cr = 52.4		
	F = 19.0	Cl = 35.47		Br = 79.75	I = 126.53

Specific Volumes.

I	II	III	IV	V	VI
H = 5.5	C = 11.0	Si = 30.3	Ti = 33.6	—	Sn = 40.8
	N = (?)	P = 25.3	V = 30.4 (26.0)	As = 26.3	Sb = 28.6
	O = 7.8 (12.2)	S = 22.6 (28.6)	Cr = 24.5	—	—
	F = 9.2	Cl = 22.7		Br = 28.1	I = 36.6

Ramsay (*J. C. Soc.* July 1879) has described a simple method of directly ascertaining the sp. gr. of a liquid at its boiling point with approximate accuracy, by means of which he has determined the specific volumes of a large number of substances. The results are contained in the table on p. 2128.

The specific volume of a considerable number of the bodies in this table has already been determined by Kopp, with whose results Ramsay's numbers show on the whole a satisfactory agreement. The specific volume of furfural indicates that both the oxygen atoms have the same value as in the aldehydes and ketones. Ramsay also points out that the specific volumes of the pyridine series of bases is very different from that of their isomerides in the aniline series. The specific volume of pyrroline would appear to show that it approaches the nitrils in constitution, and has little or no analogy to the pyridine group.

F. D. Brown (*Proc. Roy. Soc.* xxvi. 247) has shown, from very careful determinations of the vapour-tension and specific gravity of normal propyl iodide and isopropyl iodide, that the specific volumes of the two isomerides at corresponding temperatures—that is, at temperatures at which their vapour-tensions are equal—are not identical. The results of his observations are contained in the following table:

Vapour-tension in mm.	Boiling point of normal Iodide	Boiling point of Isopropyl iodide	Density of normal Propyl iodide	Density of Isopropyl iodide	Diff.
200	62.37°	50.50°	1.66704	1.64590	0.02114
300	73.51	61.33	1.64493	1.62359	0.02134
400	81.95	69.70	1.62808	1.60646	0.02162
500	88.84	76.44	1.61446	1.59246	0.02200
600	94.70	82.11	1.60250	1.58038	0.02182
700	99.83	87.13	1.59221	1.57035	0.02186
760	102.63	89.86	1.58670	1.56497	0.02196

It will be seen from the above numbers that the density of the normal iodide is greater than that of the iso-iodide by an almost constant quantity—a fact which is in accordance with our dynamical hypotheses of the constitution of matter. The normal iodide is more stable than the iso-compound, the comparative instability of the latter compound being due, in all probability, to the greater mean distance between the molecules.

Schröder (*Ber.* xiii. 1560) has also pointed out that isomerides do not invariably possess the same specific volume. It appears that the volume of an acid is greater than that of the isomeric ethers; also that the volume of a normal compound is greater than that of the secondary compound, and that the boiling point and volume of such isomeric ethers as methyl acetate and ethyl formate are greater in the case of the ether containing the acid radicle possessing the smaller molecular weight.

	B. p.	Sp. gr. at b. p.	Sp. vol. Obs.	(Kopp)	Sp. vol. Calc.
Amylene, C^8H^{10}	35°	0·6319	110·8	—	110
Hexane, C^6H^{14}	60·8	0·6199	138·7	—	143
Heptane, C^7H^{16}	91	0·6060	165·0	—	165
Benzene, C^6H^6	80	0·8142	95·8	95·9	99
Toluene, C^7H^8	111	0·7650	120·5	—	121
Xylene, C^8H^{10}	132-4	0·7335	144·5	—	143
Ethyl alcohol, C^2H^6O	78	0·7339	62·7	61·8	62·8
Octyl " $C^8H^{18}O$	181	0·6589	197·3	—	194·3
Ethyl glycol, $C^2H^6O^2$	195	0·9444	65·6	—	70·6
Acetic aldehyde, C^2H^4O	21	0·7771	56·6	56·0	56·2
Furfural, $C^5H^4O^2$	162	0·9310	103·0	—	101·4
Ethyl oxide, $C^2H^{10}O$	34·5	0·6956	106·4	106	106·8
Acetic acid, $C^2H^4O^2$	113	0·9325	64·3	63·7	64·0
Valerianic acid, $C^5H^{10}O^2$	195	0·7569	134·7	130·2	130·0
Methyl formate, $C^2H^4O^2$	33	0·9482	63·2	63·4	64·0
Ethyl formate, $C^2H^6O^2$	55	0·8649	85·6	85·7	86·0
Phenol, C^6H^6O	186	0·8789	106·9	103·8	106·8
Carbon tetrachloride, CCl_4	—	1·4658	105·0	105·6	102·2
Chloroform, $CHCl_3$	—	1·3954	85·6	85·2	84·9
Ethyl chloride, C^2H^5Cl	—	0·8510	75·8	72·8	72·3
Butyl chloride, C^4H^9Cl	—	0·8094	114·3	—	116·3
Amyl chloride, $C^5H^{11}Cl$	—	0·7801	136·5	136·2	138·3
Ethylene dichloride, $C^2H^4Cl^2$	—	1·1356	87·2	85·5	89·6
Ethylidene dichloride, $C^2H^4Cl^2$	—	1·1070	89·5	89·0	89·6
Benzoyl chloride, C^7H^5Cl	—	0·9857	126·3	136·0	139·5
Amyl bromide, $C^5H^{11}Br$	—	1·0502	143·8	149·2	143·3
Methyl iodide, CH_3I	—	2·1905	64·8	65·4	65·0
Chromyl dichloride, CrO_2Cl^2	117	1·7538	88·4	—	—
Carbon disulphide, CS^2	43	1·2176	62·3	62·3	62·6
Sulphur chloride, S^2Cl^2	138	1·4848	90·9	91·4	91·6
Sulphur, S	446	1·4799	21·6	—	—
Aniline, C^6H^5N	183	0·8527	109·1	106·6	—
Toluidine, C^7H^7N	197	0·8302	128·9	—	—
Dimethylaniline, $C^8H^{11}N$	190	0·7941	152·4	150·6	—
Diphenylamine, $C^{12}H^{11}N$	310	0·8293	203·8	—	—
Pyridine, C^5H^5N	117	0·8617	91·6	—	—
Picoline, C^6H^7N	134	0·8197	113·4	—	—
Lutidine, C^7H^9N	154	0·7916	135·1	—	—
Collidine, $C^8H^{11}N$	173	0·7839	157·9	—	—
Pyrroline, C^4H^7N	133	0·7276	92·1	—	—
Azobenzene, $C^{12}H^{10}N^2$	293	0·8256	220·4	—	—
Propionitril, C^3H^5N	97	0·7017	78·4	77·2	—
Benzonitril, C^7H^5N	192	0·8330	123·7	121·7	—
Ethyl nitrate, $C^2H^5NO^3$	87	0·9991	91·1	90·1	—
Nitrobenzene, $C^6H^5NO^2$	220	1·0210	121·5	123·8	—

(2) *Of Solids. Specific Volumes of Sulphates and Selenates.*—Pettersson (*Ber.* ix. 15 '9) finds (1) that in the series of sulphates and selenates of K, Am, Rb, Cs, the spec. vol. is regularly increased by 6·6 when the group SO^4 is exchanged for the group SeO^4 ; and (2) that the substitution of Am, Rb, Cs, for K produces an increase of volume of 9, 8, 23 in the selenates, as in the sulphates; and (3) the same regularity of increased volume shows itself in the double salts. Sodium-aluminium selenate has a smaller volume than the sulphate, a relation without example in the whole series of sulphates and selenates; thallium-aluminium selenate exhibits the opposite anomaly. The difference is possibly due to the molecules of the water of crystallisation in these two alums not being in the same state of condensation as in the other alums. The volume of a dehydrated alum exactly equals the sum of the volumes of its components.

Specific Volume of Water of Crystallisation.—Thorpe and Watts (*Chem. Soc. J.* 1880, 102) have determined the specific volumes of a number of the so-called magnesian sulphates combined with different proportions of water. The experimental results are as follows:

Copper Sulphate :

Hydrate	CuSO_4	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
Sp. gr.	3.606	3.289	2.953	2.663
	$\text{CuSO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$		
	2.645	2.284		

Magnesium Sulphate :

Hydrate	MgSO_4	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Sp. gr.	2.709	2.445	2.373	1.734	1.678

Zinc Sulphate :

Hydrate	ZnSO_4	$\text{ZnSO}_4 \cdot \text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$
Sp. gr.	3.623	3.284	2.958	2.206
	$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$		
	2.072	1.964		

Nickel Sulphate :

Hydrate	NiSO_4	$\text{NiSO}_4 \cdot \text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
Sp. gr.	3.418	3.051	2.031	1.949

Cobalt Sulphate .

Hydrate	CoSO_4	$\text{CoSO}_4 \cdot \text{H}_2\text{O}$	$\text{CoSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$	$\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$
Sp. gr.	3.444	3.125	2.668	2.327	2.134
	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$			
	2.019	1.918.			

Manganous Sulphate :

Hydrate	MnSO_4	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	$\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{MnSO}_4 \cdot 3\text{H}_2\text{O}$
Sp. gr.	3.282	2.845	2.526	2.356
	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$		
	2.261	2.103		

Ferrous Sulphate :

Hydrate	FeSO_4	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Sp. gr.	3.346	2.994	2.773	2.227

These numbers, together with those obtained by previous investigators, afford the following table of specific volume :

Hydrate	0	1	2	3	4	5	6	7
Copper sulphate .	44.4	54.3	67.0	80.0	—	109.1	—	—
Magnesium sulphate .	44.8	55.6	67.0	—	—	112.4	130.8	146.6
Zinc sulphate .	45.6	54.7	66.6	—	—	113.7	130.2	146.8
Nickel sulphate .	44.6	56.5	—	—	—	—	129.0	144.6
Cobalt sulphate .	44.7	55.2	70.9	—	97.4	114.6	130.1	146.0
Manganous sulphate .	45.0	55.7	73.6	86.6	98.2	114.4	—	—
Ferrous sulphate .	44.5	56.2	67.7	—	100.5	—	—	146.7
Mean of means	44.8	55.5	68.8	83.3	98.7	112.9	130.0	146.1

On comparing the foregoing observations, it is evident that the anhydrous sulphates of copper, magnesium, zinc, nickel, cobalt, manganese, and iron have identical specific volumes ; or, since we may define specific volume as the volume in cubic centimetres occupied by the equivalent of the salt in grams, it follows that equivalent quantities of these different sulphates occupy the same bulk in space. A like conclusion as regards certain of these anhydrous sulphates has already been drawn by Playfair and Joule. It appears too that in the case of the magnesian sulphates the volume occupied by the several molecules of water varies with the degree of hydration. The first molecule of water, the constitutional water, called water of halhydration by Graham, occupies considerably less bulk than the remaining molecules ; its mean relative value is 10.7. Each additional molecule appears to occupy a gradually increasing volume. The difference between the monohydrate and dihydrate is 13.3 ; between the dihydrate and trihydrate it is 14.5 ; between the trihydrate and tetrahydrate it is 15.4, and between the hexhydrate and heptahydrate it is 16.2.

For Schröder's papers on the volume-constitution of solids, see *Ber.* x. 848 ; *Pogg. Ann.* clx. 199-219 ; also *Ber.* xi. 1109-1116 and 1142-1146 ; *J. pr. Chem.* [2], **xix.** 366-294.

T. E. T.

W

WAGNERITE. A specimen of this mineral from Radelgrafen, near Werfen, in Salzburg, has been examined by F. v. Kobell (*J. pr. Chem.* [2], v. i. 295). It occurs in closely packed parallel prisms with deep vertical striation. Prismatic angle = 120° – 121° . Cleavage imperfect. Dissolves, though slowly, in hydrochloric, nitric, and sulphuric acids. Analysis gave:

P ² O ⁵	MgO	CaO	Na ² O, K ² O	Fe ² O ³	Al ² O ³	F	H ² O
40.30	32.78	2.24	5.12	8.00	1.11	10.00	0.50 = 100.05

from which the essential part of the mineral appears to have the composition $2\text{Mg}(\text{PO}_4)^2 + \frac{2}{3}\text{Na}^2\left\{\text{F}^2\right\}$, the double atom Na² replacing Ca isomorphously. The presence of the alkalis appears to have been overlooked by Fuchs and Rammelsberg (iv. 509).

WALPURGIN. $5\text{Bi}^2\text{O}_3, 3\text{U}^2\text{O}_3, 2\text{As}^2\text{O}_3 + 10\text{H}^2\text{O}$. See URANIC ARSENATES (vii. 1191).

WAPPLERITE. A calcium arsenate, $2\text{CaO}, \text{As}^2\text{O}_3 + 8\text{H}^2\text{O}$, or $(\text{Ca}^2\text{H}^2)\text{AsO}_4 + 7\text{H}^2\text{O}$, having part of the lime replaced by magnesia. It occurs at Joachimsthal in crystalline crusts resembling hyalite, in small botryoidal or dendritiform aggregates, and in crude vitreous deposits. It is white and translucent in the mass, limpid in separate crystals. The crystals, mostly grouped in rows, are monoclinic, very small, and exhibit various faces, and an augitic or wolframic habit; they have a bright vitreous lustre, and cleave parallel to the clinodiagonal. Sp. gr. = 2.48. Hardness = 2–2.5. Analysis gave:

	CaO	MgO	As ² O ³	H ² O
(1)	14.19	8.29	47.70	29.40 = 99.58
(2)	15.60	7.35	47.69	29.49 = 100.13

The formula above given requires 23.04 CaO, 47.33 As²O³, and 29.63 water. The mineral gives off 5 mol. (18–20 per cent.) water at 100° , and the remainder at 360° , no further loss of weight occurring at a higher temperature. At 100° it is converted, like pharmacolite, $(2\text{CaO}, \text{H}^2\text{O})\text{As}^2\text{O}_3 + 5\text{H}^2\text{O}$, which at this temperature loses 3 mol. water (11–12 per cent.), into haidingerite, $(2\text{CaO}, \text{H}^2\text{O})\text{As}^2\text{O}_3 + 2\text{H}^2\text{O}$.

Wapplerite appears also to occur in Saxony, certain specimens of hydrated calcium arsenate from Schnoeburg and Johann-Georgenstadt, regarded by Breithaupt as haidingerite, most probably belonging to this species.

The crystals have been accurately measured by Schrauf (*Jahrb. f. Min.* 1875, 290), who also finds them to be monoclinic with the axial ratio $a : b : c = 0.9125 : 1 : 0.2660$ and the axial angle $ac = 95^{\circ} 25'$. Observed faces ∞P_{∞} , ∞P_2 , ∞P , ∞P_2 , ∞P_{∞} , P_{∞} , $3P_{\infty}$, $+2P_2$, $-2P_2$, $+2P_3$, $+2P_4$, $+4P_4$, $-4P_4$. The prism-zone is mostly predominant; the faces $-2P_2$ and $-4P_4$ occur but seldom. The crystals are rarely symmetrical, single quadrants with irregular hemisymmetric development of faces, or rather confused groups of crystals, more frequently projecting from the crystalline crusts.

From pharmacolite, which accompanies it, wapplerite is essentially distinguished by its conchoidal fracture and greater hardness = 3 to 3.5.

The crystals of calcio-magnesian arsenate called *roesslerite* (v. 114), which were first described by Haidinger, in 1825, as occurring, together with haidingerite and pharmacolite, and were found by Turner (*Pogg. Ann.* vi. 193) to contain 29.06 and 34.06 per cent. water, appear, from their form and composition, to be nothing but wapplerite metamorphosed by the addition of a small quantity of magnesia and 1 molecule of water.

WARRINGTONITE. A basic cupric sulphate, $3\text{CuH}^2\text{O}^2, \text{CuSO}_4, \text{H}^2\text{O}$, from Cornwall, belonging to the brochantite group (p. 349).

WARWICKITE. This mineral, occurring at Warwick, in New York (v. 1009), has been re-examined by J. L. Smith (*Sill. Am. J.* [3], viii. 432), who finds it to have the composition A, agreeing nearly with the formula $5\text{MgO}, 3\text{B}^2\text{O}_3 + (\text{MgO}, \text{FeO}), 2\text{TiO}_2$ (B):

	B ² O ³	TiO ²	MgO	FeO	SiO ²	Al ² O ³	Sp. gr.
A.	27.80	23.82	36.80	7.02	1.00	2.21 =	98.65
B.	30.57	23.58	35.36	10.49	—	— =	100

WATER. *Distance between the Molecules of Liquid Water.*—Herwig (*Ann. Phys. Chem.* [2], iv. 465) finds that the quantity of electricity required for the complete charging of a platinum-water-cell to the potential difference of 1 volt is equal to 0.000186 farad, when the plates have a surface of 1 square cm. This value is independent of the distance between the plates and of the external resistance. In order to derive from this the charging value for a potential difference of 1.7 volt, it is necessary to multiply by (1.7×1.25) , which gives 0.000395 farad. By means of this value and the application of the theory of rotary electrolytic molecules (*Ann. Phys. Chem.* [2], 566, iv. 187) Herwig has determined directly the distance between the molecules of water, and finds it to be at most $\frac{186}{1,000,000,000}$ mm.

Lorenz (*Pogg. Ann.* cxl. 644) found by a similar, although less direct method, the superior limit, $\frac{100}{1,000,000,000}$ mm; and W. Thomson (*Nature*, 1870), by an entirely different method, $\frac{50}{100,000,000}$ mm. (*Chem. Soc. J.* xxxvi. 194).

Compressibility.—Amaury and Descamps (*Compt. rend.* lxxviii. 1564) have obtained 0.0000457 as the coefficient of compressibility at 15°, Cailliet (*Compt. rend.* lxxv. 77) observed 0.0000451 at 8°. These numbers agree almost exactly with those previously obtained by Grassi. The addition of 5 per cent. of salt diminishes the compressibility to .0000419; with 15 per cent. it is .0000356; with 30 per cent. it is .0000306.

Buchanan (*Chem. Soc. J.* xxxiv. 452) has determined the relative apparent compressibility of sea-water and of a 4 per cent. solution of sodium chloride at different temperatures, the compressibility of distilled water at the same temperature being taken as unity.

Relative Apparent Compressibility.

Temp. C.	Sea-water	4 per cent. NaCl sol.	Distilled water
26.5°	0.9360	0.9051	1
25.8	0.9191	0.8813	1
22.8	0.9214	—	1
22.1	0.9283	0.8661	1
13.7	0.9264	0.8684	1
13.3	0.9203	—	1
2.5	0.8950	—	1

Point of Maximum Density.—Exner has redetermined the point of maximum density of water according to the method of Despretz, substituting a thermo-pile of peculiar construction for the ordinary mercurial thermometer. Five series of observations gave forty-one independent values, of which the mean was 3.945°, the maximum difference being only 0.082°. This value agrees exactly with that of Playfair and Joule. The following table has some historical interest, as showing the determinations hitherto recorded:

3.945 Exner.	3.68 Neumann (<i>Jahresb.</i> 1861, 60).
4.07 Rossetti (<i>Jahresb.</i> 1867, 45).	3.46–4.04 Pierre (<i>Ann. Chim. phys.</i> [3], xiii.)
4.08 Kopp (<i>Jahr.</i> 1847–48, 66).	3.40–4.85 Hallström (<i>Pogg. Ann.</i> i.)
4.00 Despretz (<i>Ann. Chim. phys.</i> [2], i. 70).	3.47–4.38 Rumford (<i>Phil. Trans.</i> 1792).
3.945 Joule and Playfair (<i>Pogg. Ann.</i> lxxi.)	3.33–4.16 Ilpo (<i>Edin. Soc. Trans.</i> 5, 1805).
3.87 Hagen (<i>Jahresb.</i> 1856, 49).	4.35 Tralles (<i>Gibb. Ann.</i> xxvii.)
3.8 Plücker and Grissler (<i>Jahresb.</i> 1862, 50).	3.6–3.9 Eckstrand (<i>Viss. Acad.</i> 1819).

Thermal Conductivity.—The thermal conductivity of water for heat in absolute measure has been determined by A. Winkelmann (*Pogg. Ann.* cliii. 481) to be 0.00154 in square centimeters per second. Bottomley (*Proc. Roy. Soc.* xxviii. 462), by a method devised by Thomson, originally obtained values varying from .0022 to .00245; in later experiments (*Proc. Roy. Soc.* xxxi. 300) he has obtained numbers more nearly in accord with those of Winkelmann, viz. .00134 and .00154.

Specific Heat.—Baumgartner has recently redetermined the specific heat of water at 100° by the method of mixtures (*Ann. Phys. Chem.* [27], viii. 648). The following table shows the value obtained, together with those of previous observers, the specific heat at 0° being taken as unity:

Regnault	1.0130	Henrichsen	1.0720
„ recalcd. by Bosscha	1.0220	Jamin and Amaury	1.1220
Münchhausen	1.0302	Marie Stame	1.1255
Baumgartner	1.0307		

Lowering of the Freezing Point by Pressure. See Dowar (*Chem. News*, xlii. 1, 2).

Existence of Ice at Temperatures far above its ordinary Melting Point.—Carnelley (*Proc. Roy. Soc.* xxxi. 284) has made the remarkable observation that ice heated in the Torricellian vacuum under such circumstances that the pressure in the containing vessel is maintained below 4.6 mm.—i.e. the tension of aqueous vapour at the freezing point—may have its temperature raised many degrees above its ordinary melting point without liquefying. The ice, under these conditions, passes directly to the gaseous state without intermediate liquefaction. In this respect ice is analogous to arsenic, which, under ordinary pressures, passes directly from the solid to the gaseous state on heating; on increasing the pressure the arsenic fuses. Carnelley has made similar experiments with mercuric chloride, which, under ordinary pressure, melts at 288°, resolidifies at 270°–275°, and boils at 303°; on reducing the pressure to 420 mm. the boiling point falls to 275°, when the mercuric chloride begins to solidify, and at 270° becomes completely solid, the pressure being 376 mm.

The experiments of Lothar and Meyer (*Ber.* xiv. 718), Hannay and McLeod, however, render it almost certain that the ice is actually at no higher temperature than that of its ordinary melting point, and it is not improbable that the higher thermometer readings observed by Carnelley were due to the action of radiation on the exposed ball, that is, when it is denuded of ice by volatilisation. De la Rivière and van Hasselt also were unable to observe that the ice could be raised above 0°, so long as care was taken to keep the thermometer bulb covered with ice.

Absolute Boiling Point.—Mendeljeff calculates the absolute boiling point of water, the temperature corresponding to the critical point of Andrews, to be 580°.

Thermal Expansion.—The coefficient of thermal expansion of a liquid is, as a rule, diminished by pressure and increased by dilatation. The behaviour of water is, however, anomalous in this respect, as its coefficient of expansion is found to increase with compression; it must follow, therefore, that the temperature of its maximum density diminishes with pressure. This conclusion has been experimentally verified by Van der Waals.

Thermal Expansion of Sea-water.—It is well known that the addition of saline matter to water alters both its rate of thermal expansion and its point of maximum density. Thorpe and Rücker (*Phil. Trans.* clxvi. 405) have recently studied the behaviour of sea-water in this respect, as a knowledge of the law of its expansion by heat is of great importance in relation to oceanic circulation and the distribution of ocean currents. The expansion of Atlantic Ocean water, of sp. gr. 1.02807 at 0°, compared with distilled water at the same temperature, was found to be expressed between 0° and 36°—the limits of the observations—by the formula:

$$V = 1 + 0.000057682t + 0.0000060715t^2 - 0.000000032983t^3.$$

In order to study the effect of different degrees of salinity on the thermal expansion, a portion of the water was concentrated, and a second portion was diluted with different amounts of pure water, and the rate of dilatation again determined, with the following results:

Specific gravity, 1.033015 at 0°:

$$V = 1 + 0.000081272t + 0.0000050987t^2 - 0.000000018227t^3.$$

Specific gravity, 1.024915 at 0°:

$$V = 1 + 0.000040939t + 0.0000062559t^2 - 0.000000033167t^3.$$

Specific gravity, 1.020755 at 0°:

$$V = 1 + 0.000024955t + 0.0000066723t^2 - 0.000000039065t^3.$$

The authors have investigated a formula, based upon these expressions, for the expansions of these solutions, which should embrace them all as particular cases of a relation between the temperature, volume, and salinity of sea-water, as measured by its specific gravity at 0°, and in the following table are given all the data necessary to calculate the specific gravity of sea-water of any degree of salinity at any temperature between 0° and 36°. Column II. contains the specific gravities at the temperatures given in column I. of a solution the specific gravity of which, at 0° C., is 1.02000; column III. contains the numbers which must be subtracted from those in column I. for each increase of 1° over the temperatures opposite to which they are placed; and column IV. the numbers which must be added for each increase of .00001 of the specific gravity of the solutions at zero. At the head of columns III. and IV. are the number of ciphers which must be prefixed to the figures written in them in the unit place:

Temp. ° C.	Sp. gr.	Prop. parts for 1° C.	P. parts for ·0001 incr. in sp. gr.	Temp. ° C.	Sp. gr.	Prop. parts for 1° C.	P. parts for ·0001 incr. in sp. gr.
		·0000	·0000			·0000	·0000
0	1·02000	3	1	19	1·01740	25	·944
1	1·01997	4	·995	20	1·01715	25	·943
2	1·01993	5	·990	21	1·01690	26	·941
3	1·01988	6	·984	22	1·01664	27	·940
4	1·01982	8	·982	23	1·01637	28	·938
5	1·01974	9	·979	24	1·01609	29	·937
6	1·01965	11	·975	25	1·01580	29	·935
7	1·01954	12	·972	26	1·01551	30	·934
8	1·01942	13	·969	27	1·01521	30	·932
9	1·01929	14	·966	28	1·01491	31	·930
10	1·01915	15	·963	29	1·01460	32	·928
11	1·01900	17	·961	30	1·01428	32	·925
12	1·01883	17	·958	31	1·01396	32	·922
13	1·01866	19	·956	32	1·01364	33	·919
14	1·01847	20	·954	33	1·01331	33	·915
15	1·01827	21	·952	34	1·01298	33	·912
16	1·01806	21	·950	35	1·01265	34	·908
17	1·01785	22	·948	36	1·01231	34	·903
18	1·01763	23	·946				

The use of this table will be evident from the following example: *Given the sp. gr. of a sample of sea-water at any temperature t , to find it at 0° C.* Look out in col. I. the figures giving the number of entire degrees of temperature; multiply the fraction (if any) by which the observed temperature exceeds that number by the corresponding number in col. III., and subtract the result from the corresponding number in col. II. Subtract the difference from the observed specific gravity, and divide the number so obtained by that corresponding to the observed temperature in col. IV. (without prefixing the ciphers at the top of the column); add the quotient to 1·02000, and the sum will be the sp. gr. required.

Sp. gr. observed at 18·5 = 1·02475. To find it at 0° C., number opposite in col. III. is ·00023, which, multiplied by ·5, is ·000115; and 1·017630 - ·000115 = 1·017515. Subtract this from the observed sp. gr. 1·024750 - 1·017515 = ·007235. Divide by ·945, and the quotient is ·00765, which, added to 1·02000, gives 1·02765 as the sp. gr. at 0° C.

• *Pure Water.*—Absolutely pure water can only be obtained, according to Stas (*Recherches sur les Rapports reciproques des Poids atomiques*), by mixing a cold saturated solution of potassium permanganate, rendered strongly alkaline by pure potash, with ordinary distilled water, redistilling in platinum vessels, and collecting the distillate when about $\frac{1}{20}$ th has passed over.

Action of Water upon Metals.—The action of water upon metals generally is greater than is usually supposed. That it acts upon lead is of course well known; the conditions which influence this action have recently been made the subject of careful study by Muir. In the case of this particular metal its solvent action seems to be largely dependent upon the presence of free carbonic acid; agitated waters containing comparatively large quantities of carbonic acid under pressure are found to act rapidly upon lead and its alloys. From this cause the soda-water in gazogenes and syphons is liable to be contaminated with the metal. Bischof has shown (*Chem. Soc. J.* xxxi. 428) that the 'composition' tube, which is employed by plumbers, and is an alloy of lead and antimony, is even more rapidly acted upon by ordinary water than tubes of soft lead. Carnelley (*Chem. Soc. J.* xxx. 1) has observed that pure water dissolves appreciable quantities of copper, thus confirming the statements of Reichart and Roux. Carnelley finds that the weight of copper dissolved by the action of distilled water is increased by the time of exposure and by the extent of metallic surface exposed; on the other hand, it is diminished by the presence of a more positive metal, as in the case of solder, and also, by rise of temperature. The quantity of water in contact with a fixed amount of copper seems to have little or no effect upon the proportion dissolved. In the case of water containing salts in solution it is found that, with the exception of the ammoniacal salts, which appear to exert a strong specific

action, the nature of the base has only a comparatively small effect, the action of the salt depending chiefly on the nature of its acid radicle. The following is the order of action of certain of these combined acid radicles, beginning with that which has the least: nitrates, sulphates, carbonates, and chlorides. The order of this action is very different in the case of lead; in this case nitrate exerts by far the strongest effect, whilst that of carbonates and sulphates is almost nil.

Production of Ozone by Pulverisation of Water.—Leuder has already noticed that in the concentration of brine at Kissingen by the method of graduation the air in the immediate neighbourhood of the columns readily gives the ozone reaction, and Gorup-Besanez found that the quantity of ozone which is produced by a spray of water issuing under pressure depended upon the rate of evaporation. Morin and Monte have obtained similar results from experiments made by douche sprays in bathing establishments. Bellucci found relatively large quantities of ozone (or some substance giving the ozone reaction) in the air in the immediate neighbourhood of the falling water of the Falls of Terni. The production of ozone under these conditions is ascribed to the electrical state of the air induced by the friction of minute drops of water (compare p. 1479).

Contrary to the statement of Schönbein, it appears that ammonium nitrite is never formed by the evaporation of pure water in contact with nitrogen; when produced naturally it is due to the reaction of atmospheric hydrogen dioxide and ammonia.

Ammonia in Rain-water.—Lévy (*Compt. rend.* xci. 94) finds that although individual analyses of rain-water, collected from different quarters of Paris, show varying proportions of ammoniacal nitrogen, the mean monthly and yearly results are sensibly identical. The quantity of nitrogen decreases pretty regularly in passing from the cold to the warm season of the year, generally reaching its minimum in July; the mean result for that month in 1879 was 0.93 mgm. in 1 litre of water, and the mean for the year, with 4 recording stations, 1.17 mgm. The results of 4 years' analyses of rain-water collected at the observatory of Mont Souris give:

	Rain-gauge	Mean per litre	Nitrogen per sq. meter
1875-1876 . . .	541.5	1.98 mgm.	1074.78 mgm.
1876-1877 . . .	601.7	1.54 "	929.65 "
1877-1878 . . .	600.1	1.91 "	1149.40 "
1878-1879 . . .	655.3	1.20 "	787.32 "

Oxidation of Sewage in River-water.—Tidy (*Chem. Soc. J.* 1880, xxxvii. 268) has published a large number of analyses of river-water, viz. filtered and unfiltered Thames water; water of river Lea (filtered); of the Nile, Severn, and Shannon. As the result of his observations on these rivers and of experiments made specially on running water containing sewage, he concludes that when sewage is discharged into running water, provided the primary dilution of the sewage with pure water be sufficient, the run of a few miles, the precise distance of travel being dependent on several conditions, effects the removal of the whole of the organic impurity; and that whatever may be the actual cause of certain diseases—i.e. whether germs or chemical poisons—the *matrices morbi* which finds its way into the river at the sewage outfall is destroyed, together with the organic impurity, after a certain flow.

These observations have been critically examined by Frankland. From experiments made in conjunction with Miss Lucy Halcrow (*Chem. Soc. J.* 1880, xxxvii. 506), he concludes that if peaty matter dissolved in river-water is spontaneously oxidised at all, the process takes place with extreme slowness, and cannot be accomplished to any considerable extent in the flow of a river, the results showing that peaty matter is even less oxidisable than animal matters under the same conditions. Additional evidence upon these points is contained in the analytical results of the examination of rivers made in the course of the inquiry instituted by the second Rivers Pollution Commission in 1868.

Composition of Irish Sea Water.—Thorpe and Morton (*Chem. Soc. J.* xxiv. 506) have given the following numbers as showing the composition of the water of the Irish Channel:

One thousand grams contain—

Sodium chloride	26.43918
Potassium chloride	0.74619
Magnesium chloride	3.15083
Magnesium bromide	0.07052
Magnesium sulphate	2.06608
Magnesium carbonate	traces
Magnesium nitrate	0.00207
Calcium sulphate	1.33158
Calcium carbonate	0.04754
Lithium chloride	traces
Ammonium chloride	0.00044
Ferrous carbonate	0.00503
Silicic acid	traces

33.85946

Amount directly determined 33.85855

Sp. gr. 1.02721 at 0°
1.02484 at 15°

The total quantity of soluble salts contained in the water of the Irish Sea in the summer is rather larger than in winter, owing to the greater evaporation and diminished influx of fresh water in the former season.

The effect of the season is seen in the following table. The results of Forchhammer's numerous analyses of ocean-water are annexed for the sake of comparison:

Water of Irish Sea	Cl	SO ₄	CaO	MgO	Total salts
Absolute amount { Summer	18.735	2.187	—	—	34.082
in 1,000 grams { Winter	18.627	2.161	0.575	2.032	33.838
Relative amount { Summer	100	11.67	—	—	181.91
{ Winter	100	11.63	3.09	10.93	182.09

Water of Atlantic Ocean

Absolute amount {					
in 1,000 grams	19.865	2.362	0.588	2.199	35.976
Relative amount	100	11.89	2.96	11.07	181.10

T. E. T.

WAVELLITE. A specimen of this mineral from the county of Cork has been analysed by A. H. Church (*Chem. Soc. J.* xxvi. 110), with the following result:

P ₂ O ₅	F	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂	H ₂ O*	H ₂ PO ₄ †	X‡
32.00	2.09	37.18	trace	trace	0.19	22.15	4.30	2.09 = 100

* At 200°. † At a low red heat. ‡ Loss.

Church considers that the amount of fluorine given by the analysis is too low, also that part of the loss ought to be reckoned as fluorine. He regards wavellite as a fluophosphate of aluminium.

WAX. The electrical properties of wax have been investigated by W. E. Ayrton (*Phil. Mag.* [5], vi. 132). The electric conductivity of wax does not change during fusion; its specific inductive capacity rises as the temperature falls slowly from 80° to 60°, but decreases on further lowering of temperature. The refractive index of wax likewise diminishes on solidification.

The wax of *Ficus gummitlua*, used in some districts of Java as an illuminating material, has been examined by F. Kessel (*Ber.* xi. 2112). It is brown, brittle, melts between 60° and 70°, and yields to boiling water considerable quantities of a brown colouring matter, after the removal of which it is colourless. The colourless wax is resolved by ether into two bodies, one sparingly, the other easily soluble. The sparingly soluble constituent has the composition C²⁷H⁵⁶O, and is therefore isomeric with ceryl alcohol; it is crystalline, melts at 62°, is converted by PCI₃ into a chloride, and by acetyl chloride into an acetate melting at 57°. The easily soluble constituent C¹⁸H³⁰O crystallises in small nodules, melts at 73°, and likewise yields a chloride and an acetate. On subjecting the decolorised resin to dry distillation, there was obtained, together with other products, a body having the composition xC⁶H¹²O, which melted at 62°, crystallised in laminae, and was converted by oxidation with dilute nitric acid into an acid which crystallised in nodules.

British and Irish Mineral Waters.—Supplementary List (comp. v. 1017).

	Temperature	Specific gravity	Total solid contents, Parts in 100,000	Ca	Ba	Str	Mg	Na	K	Li	NH ⁴	Al	Fe	Mn	CO ²	SO ⁴	Cl	Br	I	S	NO ³	PO ⁴	SiO ²	(Organic matter)	Authority
Huel Seton, Camborne, Cornwall	33°	—	1446·21	248·50	—	—	3·66	229·77	8·41	8·05	—	18·37	0·21	—	11·13	2·14	917·84	—	—	—	—	—	3·33	—	J. A. Phillips (Proc. Roy. Soc. xxi. 139)
Royal Sulphur Well, Harrogate.	—	—	902·62	25·15	0·75	—	10·79	441·51	2·35	—	—	—	—	—	17·93	—	530·35	—	—	3·36	—	—	—	—	S. Muspratt (Chem. News, xi. 26)
Old Sulphur Well, Harrogate	10°	1011·04	1479·40	39·08	6·12	—	20·20	522·30	6·44	0·18	0·49	—	—	—	68·23	—	367·24	2·81	0·15	0·23	—	—	0·99	—	T. E. Thorpe (Phil. Mag. 1876)
Chloride of Iron Well, Harrogate.	7·2°	1005·45	683·16	48·17	5·06	0·49	20·66	155·36	2·39	trace	0·20	—	15·87	0·60	58·23	0·13	423·67	0·43	trace	—	—	—	2·01	—	C. H. Bothamley (communicated)
Ancient Alum Well, Harrogate.	—	1005·43	564·50	23·79	—	—	16·29	18·99	1·99	—	0·84	20·23	67·34	—	—	377·10	29·27	—	—	—	—	—	4·65	—	R. Hayton Davis (Chem. Soc. J. 1881, 20)
Montpellier Saline Chalybeate, Harrogate	—	—	1416·00	98·72	5·99	—	30·28	333·30	5·17	—	—	—	2·57	—	22·88	—	347·20	—	—	—	—	—	0·63	—	S. Muspratt (Chem. News, xv. 244)
Old Crescent Well, Harrogate	8·3°	—	—	6·22	—	—	3·77	63·56	9·51	—	0·03	—	—	—	38·21	9·91	89·03	—	—	0·46	—	—	1·61	1·38	Th. Fairley (Chem. News, xxx. 161)
Holy Well, Humphrey Head, Lancashire	11·6°	1005·83	714·50	42·18	0·03	0·20	15·62	196·84	5·86	0·03	0·01	—	0·15	0·01	8·02	119·60	322·40	0·04	—	—	—	0·02	1·66	—	T. E. Thorpe (Chem. Soc. J. 1868)
Tredrui, North Wales.	11°	1007·16	737·03	27·13	—	—	13·41	251·31	5·15	—	0·16	23·33	150·70	—	—	498·33	1·18	—	—	—	—	0·91	0·25	0·03	J. Carnelley (Chem. News, xxxi. 27)
Cathkin, Rutherglen, Scotland.	—	—	50·94	1·19	—	—	0·28	20·27	—	—	—	—	—	—	38·50	—	2·79	—	—	—	—	—	0·57	—	T. W. Young (Chem. News, xxxii. 113)
Airthrey, Bridge of Allan.	9°	1008·65	842·90	136·20	—	0·36	2·35	174·80	2·86	—	—	—	0·13	—	11·48	32·42	451·90	0·33	—	—	—	0·02	—	—	W. Johnstone (Chem. News, xxxi. 88)
Moffat, Scotland.	8·7°	—	129·22	8·60	—	—	2·61	33·80	3·23	—	—	—	1·19	—	9·78	0·88	68·40	—	—	0·35	—	—	1·80	—	W. Johnstone (Chem. News, xxxi. 15)
Hertfell Spring, Moffat, Scotland	9·4°	—	54·31	2·16	—	—	0·61	0·35	—	—	—	3·53	8·93	—	4·93	36·29	0·30	—	—	—	—	—	0·50	—	W. Johnstone (Chem. News, xxxi. 15)
Ballynahinch, Ireland.	—	—	29·96	2·91	—	—	1·13	0·72	0·31	—	—	—	—	—	13·28	1·40	1·28	—	—	0·18	—	—	0·12	10·40	T. Andrews (Chem. News, xxxii. 65)

WILUEWITE. A variety of xanthophyllite from the Nikolaje-Maximilianowsk mine, near Achmatowsk, in the southern Ural. From clinoclhor it is distinguished by its greater hardness (4·5), and from xanthophyllite by the very large angle of its optic axes lying in the brachydiagonal principal section, whereas xanthophyllite is regarded as uniaxial. It occurs, together with perowskite, in chlorite-slate, possesses marked dichroism, and is similar in its crystallographic relations to mica (according to Kokscharow), being rhombic, with a tendency to the development of monoclinic hemihedral forms, and a prismatic angle which gives to the combination $\infty P. \infty \bar{P} \infty$ the form of a hexagonal prism. $a : b : c = 1 : 1.73205 : 0.70729$, or $0.5773 : 1 : 0.4926$ (c nearly $\frac{1}{2}$ of the principal axis of mica). Ordinary combination $OP. - \frac{4\bar{P}\infty}{2} + \frac{6P3}{2}$. An analysis by P. v. Nikolajew gave:

SiO ²	AlPO ³	Fe ² O ³	FeO	CaO	MgO	H ² O
16.90	43.55	2.31	0.33	13.00	17.47	5.07 = 98.63

WINE. On the natural constituents of wine see A. Dupré (*Chem. News*, xxxi. 125, 137).^{*}

The composition of a considerable number of Italian wines (520 samples) from the Vienna Exhibition has been examined by Sestini, Del Torre a. Baldi (*Ber.* vii. 1294). The mean proportion of alcohol in these wines is between 13 and 14 per cent.; a few contain less than 10 per cent. The quantity of free acid, even in the sourest (the Venetian) wines, does not exceed 1 per cent. The amount of solid residue is greater in the northern than in the southern wines. The average quantity of ash is 3 to 4 per cent. The quantity of sugar in Sicilian wines varies from 13 to 20 per cent. The wines of Northern Italy contain only 1 to 2 per cent. sugar. The amount of tannin appears to vary inversely as that of sugar, the average proportion being 1 to 2 per cent. The greatest amount of glycerol ($\frac{1}{2}$ per cent.) is found in Sicilian wines. The proportion of volatile acids is greatest in the aromatic wines, amounting to one-fourth of the total quantity of free acids.^{*}

Analyses of *wine marc*, which had lain for 30 days in the vat with the must, and had then been well pressed, gave the following results in grams per kilogram:

	Red	White
Alcohol	58.5	39.0
Water	332.2	347.5
Dry substance at 100°	609.3	613.3
Nitrogen	1.032	1.016
Ash	71.08	60.03
Seeds	172.8	236.25
Bitartrate of potassium	83.8	81.7

• On the composition of Hungarian wines, see Wartha (*J. pr. Chem.* [2], vii. 350); of wines from the neighbourhood of Verona: G. dal Sie (*Gazz. chim. ital.* 1873, 257); of Californian wines: Merrick (*Amer. Chemist*, vi. 85); of Virginian wines: Cooper (*Chem. News*, xxxii. 160).

On the composition of the Must of wine prepared from grapes of different degrees of ripeness, see Cossa, Pecile a. Porro (*Biedermann's Centralblatt f. Agriculturchemie*, 1875, 341; *Dingl. pol. J.* cxxvii. 342; *Jahresb. f. Chem.* 1875, 1130).

Preservation.—Favourable reports on Pasteur's method of preserving wine by heating it to 60°–65° C. (vii. 1208) are given by U. Neubauer (*Dingl. pol. J.* cxxvii. 175). Red wine keeps particularly well after this treatment, but white wines, which are richer in albumin, sometimes become turbid.

On the Neutralisation of the Fr^o Acid in wine by the addition of Calcium Carbonate to the must after fermentation (Chaptal's process), see Moschini a. Sestini (*Gazz. Chim. ital.* 1873, 195; *Chem. Soc. J.* xxvi. 1275).

On the treatment of wine with Air during Fermentation, see A. Ott (*Dingl. pol. J.* clvii. 155; *Chem. Soc. J.* xxvi. 660).

On the Classification of wines, see B. Hoff (*Dingl. pol. J.* cxxiii. 451); P. Wagner (*Berichte d. landw. Versuchsstation, Darmstadt*, 1874; *Jahresb. f. Chem.* 1874, 1178); L. Weigert (*Chem. Centr.* 1878, 702; *Chem. Soc. J.* xxxvi. 290); also E. Mach (*Biedermann's Centralblatt f. Agriculturchemie*, 1879, 453; *Chem. Soc. J.* xxxvi. 1078).

On the Preparation of Red wine, see F. Kernlter (*Chem. Soc. J.* xxxvi. 681). On the pressing of red wine, Nessler (*ibid.* 681).

On the Plastering of wines, Pollacci (*Gazz. Chim. ital.* 1878, 379; *Chem. Soc. J.* xxxvi. 681, 762).

On the Changes which wine undergoes in keeping, see Berthelot (*J. Pharm. Chim.* [4], xxix. 489; *Chem. Soc. J.* xxxvi. 763).

Analysis of Wines. 1. *Estimation of Alcohol.*—E. Duclaux (*Compt. rend.* lxxviii. 251; *Ann. Ch. phys.* [5], ii. 233) estimates the amount of alcohol in wine by a method based upon the fact that when alcohol is added to water, the density and surface-tension of the liquid are diminished, and consequently the number of drops yielded by a given volume of the liquid from an orifice of constant width is increased. The instrument used for the purpose is a pipette of 5 c.c. volume. It is filled with the alcoholic liquid under examination, the drops are counted, and the alcoholic value is then determined from the tables which have been calculated for various temperatures. The alcoholic value of wines may thus be estimated with considerable accuracy without previous distillation. In these liquids the density varies very little, and is always near that of water; and as their superficial tension depends solely upon the alcohol which they contain, it is but necessary to count the drops which they yield, and refer to the tables for the result.

If to alcohol or water slight traces of an organic substance having a high molecular weight be added, such as acetic ether, butylic or amyllic alcohol, &c., the number of drops yielded by the alcohol or water rises very sensibly. A measurable effect can be produced with $\frac{1}{4000}$ th part of acetic ether. This process is thus available for detecting and approximately estimating certain substances when present in such small proportions as would not be indicated by any other method.

See further *Ann. Chim. phys.* [5], ii. 289; *Compt. rend.* lxxviii. 1159; *Dingl. pol. J.* cxxiii. 257, 261; *Chem. Soc. J.* xxvii. 1012.

Estimation of Sugar.—Réchamp (*Compt. rend.* lxxx. 967) remarks that wine, after being decolorised, slightly concentrated, and freed from acid potassium tartrate, contains, in addition to sugar, two substances possessed of optical rotatory power. The same substances affect also the quantity of copper precipitated from an alkaline cupric solution, so that the fermentation method is the only one that can be depended upon for the exact determination of the amount of sugar in wine. According to Chancel (*Compt. rend.* lxxxi. 46) these bodies are identical with the gummy substance found in wine by Pasteur (*Etudes sur le Vin*, 1866, p. 213). See also Mauné (*Compt. rend.* lxxx. 1026).

On the estimation of Glycerol in wine, see GLYCERIN (p. 873); also E. Reichardt (*Arch. Pharm.* x. [3], xi. 142; *Jahresb. f. Chem.* 1877, 1200).

Detection of Adulterations.—Elaborate memoirs were published a few years ago on the fraudulent coloration of wines by vegetable colouring matters of various kinds, e.g. extract of Brazil wood and logwood, cochineal, Portugal berries, berries of *Phytolacca decandra*, beet-root, hollyhock flowers, fuchsine, &c.; but as most of these alleged adulterations are harmless, and the extent to which they are employed appears to have been greatly exaggerated, a reference to the memoirs describing the mode of detecting them will be sufficient. See Gautier (*Bull. Soc. Chim.* [2], xxv. 435, 483, 530; *Analyst*, i. 109, 131; *Chem. Soc. J.* xxx. 330, 428); Chancel (*Compt. rend.* lxxxiv. 348; *Jahresb. f. Chem.* 1877, 1202; *Chem. Soc. J.* xxxii. 371); Griessmayer (*Dingl. pol. J.* cxxiii. 531; *Chem. Soc. J.* xxxii. 368); Vogel (*Ber.* ix. 1906); Hilger (*Dingl. pol. J.* cxxv. 310; *Chem. Soc. J.* xxxii. 928).

On the detection of Tannin in red wines by Ammonium-vanadate, see VANADATES (p. 2090).

On the examination of wines sophisticated with Glucose, see Neubauer (*Dingl. pol. J.* cxxv. 309; *Chem. Soc. J.* xxxii. 939).

WOLFRAM. See TUNGSTEN (p. 2066).

WOLLASTONITE. This mineral occurs, together with fassaite, less frequently with melanite and other minerals, in the lava of Santorin (Fouqué, *Compt. rend.* lxxx. 63; *Jahresb. f. Chem.* 1875, 1275). See VOLCANIC PRODUCTS (p. 2114).

WOOD. On the Electric Conductivity of various kinds of wood, see ELECTRICITY (p. 720).

Heat-conductivity.—The following determinations of the specific gravity and heat-conductivity of box, maple, and oak have been made by E. Lees (*Ann. Phys. Ergänzbd.* viii. 617):

	sp. gr.	Heat-conductivity.
Box, parallel to the fibres	0.790	135
Maple " " " " " " " "	0.634	192
Oak " " " " " " " "	0.621	161
Oak, perpendicular to the fibres, parallel to the annual rings	0.568	86
Maple, perpendicular to the fibres, parallel to the annual rings	0.607	85
Oak, perpendicular to the fibres and to the annual rings	0.571	75

On the Expansion-coefficients of various kinds of wood, see HEAT (p. 935).

On the Absorption-power for Water of various kinds of wood, see Maumené (*Compt. rend.* lxxvii. 943).

Composition of the Gases contained in the Cells and Vessels of Wood.—Experiments by J. Böhm (*Landw. Versuchsst.* xxi. 373) have led to the following conclusions:

1. The gas collected by boiling in water living branches containing air only, is poor in oxygen, and always contains over 30 per cent. of carbonic anhydride, whilst fresh branches, killed by hot steam and then heated up to 90° in pure oxygen for 6 to 7 hours, form very little carbonic anhydride. These results seem to show that the inner cells are but slowly killed in the first case, owing to the low heat-conductivity of the wood, and that the contained oxygen is converted into carbonic anhydride during the process.

2. The best method for extracting the air is to seal one end of the branch, immerse it in water at a low temperature, and connect the other end with a Sprengel pump.

3. In consequence of the low tension of the air in the cells of living plants, only that portion is extracted which has been absorbed by the branch whilst being cut off. Only in one case has the air obtained approximately the composition of that in the living plants. The cells of *Syringa* in a frozen branch are almost impermeable to compressed air, whilst, when they are thawed, air easily permeates them.

4. Numerous analyses show that the total percentage of oxygen and carbonic anhydride obtained from thawed branches is always less than the amount of oxygen contained in the atmosphere. During slow experiments carbonic anhydride is always formed by internal respiration. The remarkable composition of the cell-gas bears some relation to its low tension, and is evidently a consequence of the relatively easy permeability of moist membranes for carbonic anhydride.

5. During the experiment a little air is absorbed and a little gas escapes.

6. In the first portions of gas extracted, the total percentage of oxygen and carbonic anhydride is always greater than in the following portions, and is greater than the oxygen contents of the atmosphere. This is a consequence of the relatively easy permeability of moist membranes for oxygen, and of the greater absorbability of this gas by water as compared with nitrogen. The gas obtained from branches during the first five minutes often contained over 24 per cent. of oxygen.

7. *Syringa* branches which had hung for eight days during winter within a moistened cylinder, at an ordinary room temperature, gave very little gas, as was also the case with gas from thawed branches; the total percentage of carbonic anhydride and oxygen was always less than that of the atmosphere.

8. The gas obtained as quickly as possible from freshly-cut willow branches in summer contained from 9 to 12 per cent. of carbonic anhydride, showing that the cell-gas of plants in active growth is rich in carbonic anhydride.

9. The gas obtained from the roots of willow-plants always contains a total percentage of carbonic anhydride and oxygen less than that of the oxygen in the atmosphere. The cause of this must be that a part of the carbonic anhydride formed by the permeation of the air is carried away by the ascending sap-current. This agrees with the fact that gas extracted from the branches is richer in carbonic anhydride as the transpiration is more active.

Distillation at Low Temperatures.—H. B. Heill (*Ber.* x. 936) found amongst the products of distillation of wood at temperatures below 200°, as practised at a wood-vinagar factory at Brooklyn, furfural, and an orange-yellow crystalline body, agreeing in composition and properties with Scanlan's pyroxanthin (iv. 776).

On the Preservation of wood by Impregnation with various liquids, see *Dingl. pol. J.* cvii. 515; ccxv. 472; ccxviii. 370, 527; *Jahresb. f. Chem.* 1873, 1105; 1875, 1158–1160; *Chem. Soc. J.* xxvi. 1072; xxvii. 726, 728, 1189; xxviii. 491, 792; xxxii. 244.

On the manufacture of Paper from wood, see Rosenheim (*Dingl. pol. J.* ccxx. 81; *Chem. Soc. J.* xxxi. 234); also *Chem. Soc. J.* xxv. 1048; xxvi. 1069.

Wood-gum. This name is applied by J. Thomson (*J. für Chem.* [2], xix. 146) to a substance—isomeric with cellulose and identical with the 'pectin-substance' of

Poumarède a. Figuiet (iv. 364), which is obtained by the action of cold dilute caustic alkali on wood. It is most readily prepared from beech sawdust, by digesting with aqueous ammonia, washing, again digesting with caustic soda, filtering, precipitating the filtrate with alcohol, washing with alcohol, digesting with a little dilute hydrochloric acid to remove mineral matter, repeatedly washing with alcohol, and finally with ether.

As thus prepared, wood-gum is a colourless powder, insoluble in cold water, but soluble in about 50 parts of boiling water, forming a liquid which becomes opalescent on cooling, and yields a copious precipitate on addition of a drop of dilute hydrochloric acid, acetic acid, sodium chloride, caustic soda, or sodium acetate solution: it is insoluble in alcohol. No coloration is produced by addition of iodine tincture to a solution of pure wood-gum.

Wood-gum is found in the wood of leafy trees, but is not present in that of conifers: the quantity of this substance in the wood of any tree increases as the axis of the trunk or branch is approached: old wood contains smaller quantities of it than new wood. The following table shows the amount per cent. separated from different woods:

	Birch	Beech (old)	Beech (young)	Ash	Elm	Oak	Cherry
Periphery . . .	13.9	8.2	11.9	13.8	9.7	8.9	14.4
Middle . . .	19.7	15.9	11.3	15.9	10.7	12.0	15.4

Wood-oil, the volatile oil of *Dipterocarpus-balsam* or *Gurjun-balsam* (p. 918), may be recognised by the splendid violet colour produced on adding a drop of a cooled mixture of equal parts of sulphuric and nitric acid to a solution of 1 pt. of the oil in 20 pts. carbon bisulphide. This coloration is not interfered with by the presence of copaiba-balsam, and it remains permanent for several hours, whereas the similar colorations produced by cod-liver and valerian oils disappear very quickly (Flückiger, *Analyst*, i. 94).

Wood-tar. G. Thevius, by fractional distillation of large quantities of wood-tar, has obtained a series of hydrocarbons boiling below 80°, together with benzene at 80°. All these hydrocarbons are said to yield nitro-amido-derivatives, and likewise dye-stuffs (*Dingl. pol. J.* cccxvii. 374; *Chem. Soc. J.* xxxiv. 664). See further TAR (p. 1889).

WOOL. The heat-conducting power of wool is 12, that of air being taken as unity (*J. Schulmeister, Dingl. pol. J.* cccxvi. 326).

Air-dried wool contains 14.35 per cent. of water (Bernard, *ibid.* 216).

Decomposition by Barium Hydrate.—Schützenberger (*Compt. rend.* lxxxvi. 767), by decomposing 100 grams of purified wool with an aqueous solution of barium hydrate (300–400 grams) at 170°, has obtained the following products:

Nitrogen (evolved as ammonia)	5.25
Carbonic acid (separated as BaCO ₃)	4.27
Oxalic „ (separated as BaC ₂ O ₄)	5.72
Acetic „ (by distillation and titration)	3.2
Pyrrolino and volatile products	1 to 1.5
Elementary composition of fixed residue, containing leucine, tyrosine, and other nitrogenous products	{ C . . .	47.85
	{ H . . .	7.69
	{ N . . .	12.63
	{ O . . .	31.83
		100.00

Oxidation in Alkaline Solution.—Wool, dissolved in aqueous potash and oxidised by potassium permanganate is converted into cyanopropionic acid, C³H⁴(CN)O² (Wanklyn a. Cooper, p. 1676).

Bleaching.—The following directions for the bleaching of wool are given in Reiman's *Farbezeitung*, 1873, No. 31. One hundred kg. wool are treated with a solution of 5 kg. acid sodium sulphite, and 2 kg. hydrochloric acid are added; or the wool is sprinkled with the solution of the same quantity of the salt in 100 litres of water and then dipped in a bath of hydrochloric acid.

J. Persoz (*Monit. scient.* [3], iv. 862) discusses the difficulties which have to be overcome in the bleaching of wool. The sulphurous acid, either gaseous or in aqueous solution, unites with the colouring matters of the wool, forming colourless compounds. The bleached wool consequently contains sulphurous acid, and must therefore be very carefully treated, otherwise the sulphurous acid will escape and the colours will reappear. The sulphurous acid may, by the action of atmospheric oxygen, especially if assisted by sunlight, be converted into sulphuric acid, which affects the course of

the subsequent operations (dyeing, printing), besides acting on the tissue itself. The presence of sulphurous acid destroys the faint tint usually given to bleached fabrics by aniline-dyes. *Bleu de Lyons* (dissolved in alcohol) is not altered by sulphurous acid; Nicholson's alkali-blue is darkened by it; fuchsine-violet is turned blue; *violet de Paris* is first turned blue and then disappears altogether; aniline-red is completely decolorised. *Bleu de Lyons* and fuchsine-violet are therefore the colours which best withstand the action of sulphurous acid, and should accordingly be used for the blueing of bleached wool. The water used for washing has a very great influence on the fabrics, and no cheap method has yet been discovered of preventing the injurious action which it sometimes exerts. Very great care must be bestowed on the glazing of the tissues. The smallest trace of lead-compounds in the glaze is sure, sooner or later, to exert a disturbing action. The addition of paraffin to the glaze must be avoided, as paraffin cannot be subsequently removed from the tissue. If the woollen fabric is wound on rollers, it is not advisable to lay a number of such rollers one on the other, as the tissue is thereby prevented from expanding and contracting freely, and consequently becomes dragged. The rolls should be as far as possible set up on end and frequently reversed; otherwise the water will collect at one end, thereby causing the cloth to dry unequally and become spotted. On the whitening of woollen cloths see also V. Preston (*Dingl. pol. J.* cccxv. 531; *Jahresb. f. Chem.* 1877, 1229), and A. Kiemeyer (*Dingl. pol. J.* cccxv. 389).

Dyeing.—According to C. Lauth (*Bull. Soc. Chim.* [2], xix. 401), wool may be prepared for dyeing with aniline-green by treating it with sodium thiosulphate and an acid. The sulphur thereby separated fixes itself on the wool and imparts to it the power of taking up the aniline-green. Direct experiments have shown that this action is exerted only by that portion of the sulphur which is insoluble in carbon bisulphide. Every other method of impregnating wool with sulphur has led to only negative results. It is advantageous to mix the thiosulphate solution with alum or a zinc salt. If it be desired to give the green a tinge of yellow by simultaneous dyeing with picric acid, a small quantity of zinc acetate must be added to the bath. Zinc acetate keeps up the blue tint of the aniline-green.

Alkali-blue (Nicholson's blue) may be fixed on wool, so as to stand the fulling process, by adding a little zinc sulphate to the second (acid) bath. Dyeing with other aniline colours is also greatly assisted by the addition of zinc sulphate to the dye-bath (E. Brauss, *Dingl. pol. J.* ccviii. 157).

To print a yellow colour on woollen thread previously dyed red, 40 grams of *xanthine* are dissolved in 500 g. water, and, on the other hand, 30 g. sodium sulphite are dissolved in 500 g. water, and 250 g. zinc-dust are stirred into the resulting solution. The two solutions are then mixed, the pattern is printed with the mixture, and the cloth is finally steamed. Aniline-yellow cannot be used for this purpose, since aniline-colours are destroyed by zinc-dust (*Dingl. pol. J.* ccviii. 238).

On the direct yellow-dyeing of wool with *chromic acid*, see Jacquemin (p. 460).
 • V. Jolet (*Dingl.* cccxix. 288) recommends for this purpose the use of chrome-alum instead of potassium dichromate, a greater regularity of tint being thereby obtained. The wool is boiled for an hour and a half in a chrome-alum bath, whereby it is coloured bluish-green. The colour is stable, and bears exposure, which is not the case when potassium dichromate is used. For blues and greens, alum and sulphuric acid are added to the bath; for blacks, the sulphuric acid is omitted. For brown, sulphuric acid is used if the material is not to be dyed with madder. Copper sulphate gives darker tones, whilst addition of tin salts is made in case of violet-blues and bluish-greens. 25 kilos. require the following proportions in the chrome-alum bath:

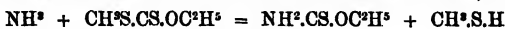
Colour	Alum. Grams	H ² SO ⁴ . Grams	CuSO ⁴ . Grams	Chrome-alum. Grams
Brown madder	—	—	—	650
Olive madder	—	—	50	630
Black	—	—	—	625
Coffee-brown	—	40	100	600
Dark blue	500	50	50	450
Light blue	500	50	—	400
Dark green	600	60	100	500
Light green	300	60	—	625
Violet	500	50	40	500

salts of tin.

On the removal of Vegetable fibres from Wool by the action of Acids (Chemical Purification of Wool) see Duclaux, Lechartier & Raulin (*Bull. Soc. Chim.* [2], xxi. 337; *Jahresb. f. Chem.* 1874, 1204; *Chem. Soc. J.* xxviii. 200). On the use of Aluminium chloride for the same purpose, see Joly (*Dingl. pol. J.* cccxvi. 328).

X

XANTHAMIDE, $\text{NH}^2\text{CS}.\text{OC}^2\text{H}^5$ (v. 491), is formed, together with methyl-mercaptan, by the action of alcoholic ammonia on the thiocarbonic ether, $\text{CH}_3\text{S}.\text{CS}.\text{OC}^2\text{H}^5$:



(Salomon a. Manitz, *J. pr. Chem.* [2], viii. 114).

On the reaction of xanthamide with *Valeral*, see p. 2084.

Methylic Xanthamide, $\text{NH}^2\text{CS}.\text{OCH}_3$, is formed, together with methylic oxythiocarbamate, $\text{NH}^2\text{CO}.\text{SCH}_3$, by the action of thiocyanic acid on methyl alcohol.

XANTHATES, $\text{C}^2\text{H}^5\text{RS}^2 = \text{RS}.\text{CS}.\text{OC}^2\text{H}^5$ (R denoting a metal or alcohol-radicle). The products of the dry distillation of metallic xanthates have been examined by Fleischer a. Hankó (*Ber.* x. 1293). The dry potassium and sodium salts yield carbon disulphide, ethyl monosulphide, ethyl disulphide, and carbon oxy-sulphide; the hydrated salts yield mercaptan, carbon disulphide, the two sulphides of ethyl, carbon dioxide, and hydrogen sulphide. The residue consists chiefly of carbonates. *Lead xanthates* yield the same products as the dry xanthates of the alkali-metals. The compound called *xanthurin*, described by Couerbe as a product of the distillation of xanthates, is regarded by Fleischer a. Hankó as a mixture of the two ethyl sulphides with carbon oxy-sulphide.

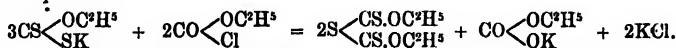
E. A. Grete (*Ber.* x. 1039) makes use of the hydrogen-sulphide evolved by the decomposition of xanthates for the reduction of nitric acid in the quantitative estimation of nitrates. For this purpose the nitrate is heated with a mixture of a xanthate and soda-lime.

On the estimation of Carbon disulphide by converting it into potassium xanthate, and titrating this salt with a normal solution of copper, see CARBON BISULPHIDE (p. 408).

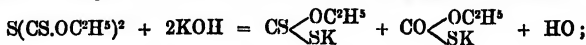
According to P. Zöller (*Dingl. pol. J.* cexxi. 191; cexxii. 190) small quantities of xanthates mixed with the soil prevent the formation of fungi. Zöller a. Grete (*Ber.* viii. 802, 955) recommend potassium xanthate as a remedy against Phylloxera.

The following xanthates are described by T. L. Phipson (*Compt. rend.* lxxxiv. 1459):—The *cuprous salt* formed on mixing a cupric salt with potassium xanthate is an orange-yellow shining precipitate, insoluble in water, easily soluble in carbon sulphide, very easily in nitric acid; in the dry state it burns like tinder. It is insoluble in ammonia, a property which may be rendered available for the separation of copper from metals which form xanthates soluble in ammonia. The xanthates of *nickel* and *cobalt* are especially distinguished one from the other by their reaction with ammonia, the former being soluble therein, the latter insoluble. The *zinc salt* is easily soluble in ammonia.

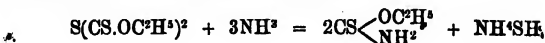
When potassium xanthate and ethyl chlorocarbonate are mixed in nearly molecular proportions, a slight excess of the former being, however, advantageous, a white precipitate is formed containing chloride and ethylcarbonate of potassium, and at the same time an oily liquid is produced, which, after treatment with a large quantity of water, solidifies to a crystalline pulp; and on recrystallising this product from alcohol, splendid yellow needles are obtained, melting at 55° and consisting of diethylic dithiodicarbthionate, $\text{S}(\text{CSOC}^2\text{H}^5)^2$, analogous to the ethylic dicarbthionate, $\text{S}(\text{COOC}^2\text{H}^5)^2$, which V. Meyer obtained by the action of sodium monosulphide on ethyl chlorocarbonate (vi. 406). Its formation may perhaps be represented by the equation:



With potassium ethylate it yields $\text{CO}(\text{OC}^2\text{H}^5)\text{SK}$, and potassium xanthate:

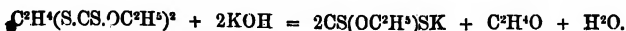


and with alcoholic ammonia it forms xanthamide:

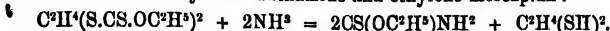


Potassium xanthate and ethylene bromide form ethylethylenic xanthate, $\text{C}^2\text{H}^4(\text{S}.\text{CS}.\text{OC}^2\text{H}^5)^2$, as a yellowish oil, which solidifies after washing with water, and

is obtained by recrystallisation from ether in fine strongly refractive crystals, apparently belonging to the rhombic system and melting at 42° . This body is decomposed by potassium ethylate, with formation of potassium xanthate, ethylene bromide, and water:



With alcoholic ammonia it yields xanthamide and ethylene-mercaptan:



The action of ethylene bromide on the compound $CO(OC^2H^3)(SK)$ appears to be analogous to that which it exerts upon the xanthate (H. Welde, *Ber.* ix. 1044).

XANTHININE, $C^4H^4N^2O^2$. This base, which Finck obtained by the action of heat on ammonium thionurate (v. 1051), is also produced by the action of sulphuric acid at 150° on pseudouric acid (p. 1698).

XANTHIUM. According to Guichard (*Pharm. J. Trans.* [3], vii. 249), *Xanthium spinosum* contains an alkaloid; Godeffroy, on the other hand (*Ber.* ix. 1796), found in it neither alkaloid, nor glucoside, nor bitter principle. The plant yields a large quantity of ash rich in alkalis and nitrates. By distillation with water it yields a distillate smelling of chamomile, from which a small quantity of a greenish oil may be separated.

XANTHOGALLOL, $C^{12}H^4Br^{14}O^6$ (Stenhouse, *Chem. Soc. J.* xxviii. 1). This compound is formed by the action of bromine in presence of water on tribromopyrogallol (vii. 1031). It is best prepared by gradually adding 1 mol. pyrogallol to 10 pts. bromine, leaving the product at rest for two or three hours to ensure the complete transformation of the pyrogallol into tribromopyrogallol, and then shaking it with 30 pts. water till it is completely dissolved, and heating it. With a larger quantity of water the yield of xanthogallol is smaller, an oil being formed at the same time, which greatly increases the difficulty of purification. Xanthogallol is formed only by the action of bromine and water on already-formed tribromopyrogallol, according to the equation:



Pyrogallol itself, when similarly treated, does not yield a trace of it.

Xanthogallol, purified by recrystallisation from carbon sulphide and light petroleum, forms shining yellow laminae, melts at 122° , and dissolves readily in ether, benzene, and carbon sulphide, less easily in petroleum. It is decomposed by solution in alcohol, by boiling with water, and by prolonged boiling with benzene or petroleum. When a solution of 1 pt. xanthogallol in 10 pts. ether is agitated with 2 pts. of a cold saturated solution of sodium carbonate, the liquid being cooled from time to time, the ether takes up a body which remains, on evaporation of the ether, in the form of an oil having a peculiar odour, whilst a sodium-compound separates in light yellow shining laminae. If this sodium-compound, after washing with a nearly saturated solution of sodium carbonate, be suspended in 8 pts. of water and dilute sulphuric acid added, a substance, apparently having the composition $C^{12}H^4Br^{14}O^6$, separates in long colourless needles melting at 130° , very easily soluble in alcohol and ether, soluble also in hot benzene and carbon sulphide, sparingly in petroleum, decomposing gradually at ordinary temperatures. The sodium-compound is not very soluble in cold water, but dissolves readily in alcohol. It is decomposed by drying at ordinary temperatures and by the boiling of its aqueous solution. The analogous ammonium and potassium compounds resemble the sodium-compound in their properties. The aqueous solution of the sodium-compound gives a dirty-white precipitate with cupric sulphate, yellow with silver nitrate. The solution of the silver precipitate in nitric acid decomposes on boiling, with separation of silver bromide. The chlorides of calcium and barium give white precipitates. The barium-compound becomes yellow when dried in a vacuum, and then contains 15.64 to 15.72 per cent. Ba. The white crystalline compound, agitated in ethereal solution with aqueous potassium iodide, yields a shining yellow precipitate insoluble in water, but dissolving, apparently with decomposition, in alcohol.

When tribromopyrogallol is treated with only 1 mol. bromine and then mixed with 5 to 10 pts. water, an orange-coloured solution is formed, which after a short time deposits colourless laminae of a compound decomposing slowly on standing, more quickly when gently heated. This compound is nearly insoluble in carbon sulphide, slightly soluble in water, easily in ether, and is precipitated therefrom in the crystalline state by chloroform or carbon sulphide. It does not appear to be converted into xanthogallol by the action of bromine in excess.

XANTHOPHYLL. See PLANT-COLOURS (p. 1630).

XANTHOPHYLLITE. On the variety of this mineral called *Wiluweit*, see p. 2137.

XANTHOPURPURIN, $C^{12}H^4O^4 = C^6H^4 \begin{smallmatrix} CO \\ CO \end{smallmatrix} C^6H^2(OH)^2$. This unsymmetrical dihydroxyanthraquinone—better called *Purpuroxanthin*, inasmuch as xanthopurpurin would seem to imply that the compound in question is a purpurin—that is to say, a tri-hydroxyanthraquinone—was discovered by Schützenberger, who obtained it from madder and by reduction of purpurin; was afterwards prepared by Liebermann a. Fischer from purpuramide by the action of nitrous acid (p. 103), and has been further examined by H. Plath (*Ber.* ix. 1204). It crystallises from glacial acetic acid in thick shining needles melting at 262° – 263° . By boiling with sodium acetate it is converted into a salt which crystallises in red needles. It forms crystalline compounds with lime and baryta.

Dibromopurpuroxanthin, $C^{12}H^4Br^2(CO)^2(OH)^2$, formed by the action of bromine at ordinary temperatures on purpuroxanthin, is slightly soluble in alcohol, easily soluble in glacial acetic acid, from which it crystallises in orange-coloured needles melting at 227° – 230° . By boiling with ammonium acetate it is converted into dibromopurpuroxanthinammonium, which crystallises in felted groups of red needles having a splendid metallic lustre.

Dinitropurpuroxanthin, $C^{12}H^4(NO^2)^2(CO)^2(OH)^2$, obtained by the action of fuming nitric acid (sp. gr. 1.48) at ordinary temperatures on purpuroxanthin, is soluble in water, more readily in ether, alcohol, and glacial acetic acid, and crystallises in small light-red needles melting at 249° – 250° . Its barium compound, $C^{12}H^4(NO^2)^2(O^2Ba)O^2$, crystallises in dark-red needles; the ammonium compound, $C^{12}H^4(NO^2)^2(OH)(ONH^4)O^2$, obtained by boiling the dinitro-derivative with ammonium acetate, forms light-yellow needles having a silky lustre. By treating purpuroxanthin dissolved in strong sulphuric acid with nitrous acid, a dinitropurpuroxanthin is obtained, which also melts at 249° , but crystallises from glacial acetic acid in thick needles having a steel-blue colour. It dissolves readily in water, alcohol, ether, benzene, and glacial acetic acid, and dyes wool an orange colour. Whether this dinitropurpuroxanthin is identical or isomeric with the former is a question not yet decided.

Dimethylpurpuroxanthin, $C^6H^4.C^2O^2.C^6H^2(OCH^3)^2$, is formed when purpuroxanthin, methyl iodide, and potassium hydroxide in molecular proportions, with addition of a little alcohol, are heated together at 100° in a sealed tube for several hours. It crystallises from glacial acetic acid in small light-yellow needles melting at 178° – 180° . *Diethylpurpuroxanthin*, prepared in like manner, forms dark-yellow needles melting at 170° , insoluble in water, easily soluble in alcohol and in glacial acetic acid.

Purpuroxanthin-carboxylic acid, $C^{12}H^4O^4 = C^{14}O^4H^2.COOH$. *ε-Purpurin*. This acid has been found by Schunck a. Römer (*Ber.* x. 172) in a substance accompanying natural purpurin, and may be obtained from the mother-liquor which remains after the crystallisation of the crude purpurin from alcohol. This mother-liquor is evaporated to dryness; the residue is treated with boiling water; a few drops of hydrochloric acid are added to the solution; the resulting precipitate is boiled with baryta-water as long as it is acted upon thereby; the insoluble barium salt of purpuroxanthin-carboxylic acid is decomposed by hydrochloric acid; and the free acid is recrystallised from alcohol. The acid may also be prepared from the aluminium-compound of commercial purpurin by exhausting this compound with boiling dilute hydrochloric acid, which leaves part of it undecomposed, and boiling this portion with strong hydrochloric acid.

Purpuroxanthin-carboxylic acid is, according to Schunck a. Römer, the chief constituent of *ε-purpurin* and identical with Stenhouse's munjistin (iii. 1061). It crystallises in hydrated yellow needles having a golden lustre, and efflorescing even on exposure to the air, more readily at 50° . It melts at 231° , and between 232° and 233° is completely resolved into carbon dioxide and purpuroxanthin. It dissolves readily in boiling hydrated alcohol, and frequently separates from the concentrated alcoholic solution in anhydrous lupinæ having a golden lustre. By very slow crystallisation from glacial acetic acid, in which it is easily soluble, it is obtained in tetrahedrons. It is more soluble in boiling water than purpurin; dissolves likewise in benzene, chloroform, ether, strong sulphuric acid, potash-ley, ammonia, boiling alum-solution, and sodium carbonate. The barium salt has a crimson colour and is insoluble in water.

XANTHOROCELLIN, $C^{21}H^{17}N^2O^2$. See ROCKELLA (p. 1759);

XANTHORHAMNIN, $C^{48}H^{66}O^{29}$. The glucoside of *Rhamnus infectorius*. See RHAMNUS (p. 1757).

XENOTIME. This mineral occurs in the Binnenthal, in small crystals of the quadratic system, exhibiting the combination $P \infty P.3P3$ (angle $P : P$ in the lateral edges = $82^\circ 22'$), and agreeing in form with the xenotime of the St. Gothard, Hitteröe, and Tavetschthal, but not with Kennigott's *wiserine* (C. Klein, *Jahrb. f. Min.* 1875, 337, 369, 852).

Xenotime from Hitteröe has been analysed by O. E. Schiötz (*ibid.* 1876, 306), with the following result:

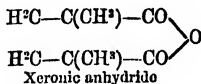
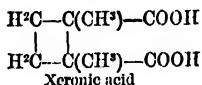
P ² O ⁵	Y ² O ³	CaO ² , Al ² O ³	Fe ² O ³	Mn ² O ³	FeO	CaO	H ² O
31.88	54.68	8.24	2.93	0.13	0.87	0.13	1.56 = 100.62

Xenotime has been prepared artificially by F. Radominski (*Compt. rend.* lxxx. 304).

XERONIC ACID, C⁸H¹⁰O⁴. A. Prehn (*Ber.* viii. 19, 359), in preparing methacrylic (crotonic) acid from citraconic anhydride, obtained, together with the calcium methacrylate, a sparingly soluble calcium salt, the acid of which boiled at 232° and remained fluid at -20° . This acid, or rather its anhydride, C⁸H¹⁰O³, which Fittig has since obtained as a product of the decomposition of citraconic anhydride (p. 513), appears to have been contained in the citraconic anhydride used in Prehn's experiments, as on dissolving the latter in water, dark oil-drops remained, which, when distilled with steam and afterwards heated with water and pulverised calc-spar, yielded the sparingly soluble calcium salt above mentioned.

Xeronic acid exhibits the peculiarity, hitherto observed only in acid anhydrides of the lactide type, of separating in the form of an anhydride when their salts are decomposed by a stronger acid, so that the acid itself is not actually known. Some of its salts have been examined by Fittig (*Liebigs Annalen*, clxxxviii. 59). The calcium salt above mentioned has the composition C⁸H¹⁰O⁴.Ca + H²O, gives off its water at 130° – 140° , and when heated with dilute hydrochloric acid yields the anhydride, C⁸H¹⁰O³, as a colourless oil, which is very slightly soluble in water, volatilises very easily with steam, may also be distilled alone, and boils without decomposition at 242° . It dissolves very slowly when agitated with cold concentrated solution of sodium carbonate, more quickly when heated, also in ammonia. The dilute ammoniacal solution, rendered neutral by evaporation, is not precipitated by calcium chloride at ordinary temperatures, but when heated therewith yields a thick white precipitate of the calcium salt. The barium salt, C⁸H¹⁰O⁴.Ba + $\frac{1}{2}$ H²O, prepared in like manner, is very much like the calcium salt; it becomes anhydrous at 140° , and undergoes no further. The silver salt, C⁸H¹⁰O⁴.Ag², obtained in a similar manner, is a white precipitate, very slightly soluble in boiling water, not affected by light.

Xeronic acid has probably the constitution of di-methylacrylic acid:



XYLENES, C⁸H¹⁰ = C⁶H⁴(CH³)². Ortho- and para-xylene occur in coal-tar. Para-xylene is obtained by agitating crude coal-tar xylene with warm common sulphuric acid, which dissolves only traces of paraxylene, treating the undissolved residue with fuming sulphuric acid, which converts it into paraxylene-sulphonic acid, and separating this acid from the crude mass by water, which throws it down in the form of a crystalline hydrate nearly insoluble in the diluted acid. The hydrated sulphonic acid thus obtained may be purified by repeated crystallisation, or by conversion into the barium or sodium salt. When subjected to dry distillation, or heated with hydrochloric acid, it yields perfectly pure paraxylene, which for the most part remains solid at 13° .

The portion of the crude xylene which is soluble in ordinary sulphuric acid is a mixture of ortho- and meta-xylenes, the latter predominating. To separate them, the sodium salts of the sulphonic acids into which the crude sulphuric acid solution is first converted, as above mentioned, are transformed by the action of phosphorus pentachloride into chlorides, and these by Schiller and Otto's method (p. 1851) into the corresponding sulphonic acids; and on crystallising the sodium salts of these acids, that of the orthoxylene-sulphonic acid separates out first, while that of the metaxylene-sulphonic acid remains in the mother-liquor.

Orthoxylene may also be obtained from the tar-oil by a shorter process, which does not involve the preparation of the sulphonic acids—namely, by saturating the portions extracted from the oil by ordinary sulphuric acid, after dilution, with calcium carbonate, converting the resulting salts into sodium salts, concentrating the solution strongly, and leaving it to crystallise. The crystals of sodium orthoxylene-sulphonate thus obtained may be purified by three recrystallisations.

Orthoxylene separated from the sodium-salt of its sulphonic acid, or from the corresponding amide, by the action of hydrochloric acid at 190°–195°, boils at 142°–143° (O. Jacobsen, *Ber.* x. 1009).

Paraxylene.—In preparing this hydrocarbon by the action of methyl iodide and sodium on parabromotoluene, b. p. 28.5° (v. 1056), it is not advisable to use ether as a diluent, as the action is then extremely violent and the product small. With benzene, on the other hand, as a solvent, the reaction takes place at ordinary temperatures, and is completed in a comparatively short time. The quantity of bromotoluene acted upon in one operation should not be greater than 50 grams. The yield never exceeds one-fifth of the bromotoluene employed, a considerable quantity of ditolyl being formed at the same time.

Pure paraxylene melts at 15°, boils at 136°–137°, and is converted by oxidation with dilute nitric acid into *paratoluic acid*, melting at 173° (Jannasch, *Liebig's Annalen*, clxxi. 79).

Metaxylene is produced, together with a small quantity of paraxylene, by passing a stream of methyl chloride, dried by sulphuric acid, for forty-eight hours into two long-necked flasks containing 500–600 gr. toluene and 15–20 per cent. aluminium chloride (see *Hydrocarbons*, p. 1063), and placed in a water-bath at 70°–80°. The product, purified by fractionation and oxidised by permanganate, or in alkaline solution by chromic acid, yields isophthalic acid, together with a small quantity of terephthalic acid (Ador a. Rilliet, *Ber.* xi. 1627).

Metaxylene is also formed, together with dimethylethylbenzene, by submitting to fractional distillation those portions of crude wood-spirit which are insoluble or only slightly soluble in acid sodium sulphite, and heating the fractions 130°–140° and 165°–175° for some time in an oil-bath with zinc chloride (80 c.c. liquid with 10 gr. zinc chloride). The clear oil floating on the top of the product gave, after washing with strong sulphuric acid and rectification over sodium—from the first portion, xylene boiling at 128°–143°; from the second, dimethylethylbenzene boiling at 175°–183°. The xylene, by oxidation with chromic acid, was converted into isophthalic acid (Kraemer a. Grodzki, *Ber.* ix. 1920).

Metaxylene, heated in a sealed tube at 130°–150° with dilute nitric acid (1 acid to 2 water), is oxidised to *metatoluic acid* (Brückner, *Ber.* ix. 405).

When *carbonyl chloride* is passed into metaxylene cooled to –15°, and aluminium chloride then gradually added to the mixture, xylal ketone, $\text{CO}(\text{C}^6\text{H}^5)^2$, is formed, which remains liquid at –60°, boils at 340°, and is converted by saponification with potash into dimethyl-benzoic acid. By prolonged boiling it gives up water, and is converted into a hydrocarbon, $\text{C}^{11}\text{H}^{16}$ (Ador a. Rilliet, *Ber.* xi. 399).

Metaxylene (1 vol.), heated for forty-eight hours at 280° with 10 vol. *hydriodic acid* and *amorphous phosphorus*, is converted into hexhydrometaxylene, C^6H^{16} (p. 160). The product, after washing with soda-ley and water, drying, and rectification over sodium at 150°, boils between 115° and 120°, has a specific gravity of 0.777 at 0° and vapour-density = 3.75. With bromine and strong sulphuric acid it reacts like a saturated hydrocarbon. The same hydrocarbon is produced by heating 1 pt. camphoric acid at 280° with 12 pts. fuming hydriodic acid saturated at 0° (Wreden, *Ber.* vi. 1379).

Chlorometaxylene, or *Metaxylal Chloride*, $\text{CH}^3.\text{C}^6\text{H}^4.\text{CH}^2\text{Cl} = \text{C}^6.\text{CH}^3.\text{H}.\text{CH}^2\text{Cl}.\text{H}^3$ (also called *Isotolyl Chloride*), is obtained by the action of chlorine on metaxylene at the boiling heat. It boils at 195°–196°, and has a specific gravity of 1.079 at 0° and 1.064 at 20° (Gundelach, *Compt. rend.* lxxxii. 1444).

Benzyl-xylene, $\text{C}^{11}\text{H}^{16} = \text{C}^6\text{H}^5.\text{CH}^2.\text{C}^6\text{H}^5(\text{CH}^3)^2$. Two modifications of this hydrocarbon, viz. benzyl-isoxylene and benzyl-paraxylene, are obtained by acting upon isoxylene and paraxylene with benzyl chloride in presence of zinc. Benzyl-isoxylene is a colourless liquid, of faint aromatic odour, boiling at 295°–296°. Benzyl-paraxylene is a similar liquid, boiling at 293.5°–294.5°. The former, when oxidised with potassium dichromate and sulphuric acid, yields benzoyl-isophthalic acid, $\text{C}^6\text{H}^5.\text{CO}.\text{C}^6\text{H}^4(\text{CO}^2\text{H})^2$ (p. 313) (Zincke, *Deut. Chem. Ges. Ber.* v. 799).

Paraxylene (1 : 4) can evidently yield but one benzyl-paraxylene, viz. that which has the structure 1 : 2 : 4 or 1 : 3 : 4; but isoxylene, 1 : 3, may yield three benzyl-isoxylenes, viz. 1 : 2 : 3, 1 : 3 : 4, and 1 : 3 : 5. Which of the three is formed by the process above mentioned there appears to be at present no means of determining.

Bromoxylenes. *Symmetrical Bromometaxylene*, $\text{C}^6\text{H}^5(\text{CH}^2(\text{CH}^3)\text{Br})_2$, is obtained by passing nitrous gas into an alcoholic solution of Genz's bromoxylidime, $\text{C}^6\text{H}^5\text{Br}.\text{NH}^2$ (vii. 1210), a dibromoxylene (b. p. 252°) being formed at the same time as a secondary product. The monobromoxylene has a specific gravity of 1.362 at 20°, remains fluid

at -20° , and boils at 204° . A mixture of this bromoxylene and ethyl bromide heated with sodium yields symmetrical ethyl-dimethyl-benzene, $C^6H^4.H.CH^3.H.CH^3.H$ (Wroblewsky, *Ber.* ix. 495). See p. 751.

Bromoparaxylene, $C^6H^4.Br.H.CH^3.H^2$, prepared by dropping bromine into well-cooled paraxylene, boiling the well-washed product with alcoholic potassium sulphide, and rectifying, boils at 199.5° – 200.5° , and solidifies on cooling in shining laminae or tables melting at 10° . By oxidation with chromic acid in glacial acetic acid solution it is converted into parabromotoluic acid melting at 203.5° . By nitration it yields a liquid which after a while deposits crystals, melting, after pressure and recrystallisation from alcohol, at 70° – 71° (Jannasch).

Nitroxylenes. According to A. Rammer (*Bull. Soc. Chim.* [2], ix. 434), the portion of crude xylene insoluble in sulphuric acid (*p*-xylene) yields a dinitro-xylene, which melts at 92° , and, according to measurements by Descloizeaux, forms monoclinic crystals, whereas the xylene soluble in sulphuric acid (*o*-xylene) yields the other dinitroxylene described by Glinzer a. Fittig (v. 1058), which melts at 123.5° . According to Jannasch (*Liebig's Annalen*, clxxi. 79), paraxylene treated with fuming nitric acid in the cold yields both these dinitro-derivatives, which separate at once as a solid product, whereas Glinzer a. Fittig obtained an oil from which the dinitro-compounds crystallised out after some time.

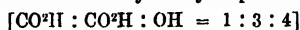
XYLENESULPHAMIDES, $C^6H^4(CH^3)_2.SO^2NH^2$ (Jacobsen, *Ber.* ix. 256; x. 1014; xi. 17). Two *metaxylenesulphamides*, distinguished as α and β , are obtained from the mother-liquors of the preparation of pseudocumene and mesitylene respectively (pp. 1283, 1285): α -*metaxylenesulphamide* [1 : 3 : 4], or $C^6H^4.H.CH^3.SO^2NH^2.H^2$, crystallises from hot alcohol in large shining laminae, from hot water in long pointed needles, and melts at 137° ; β -*metaxylenesulphamide* [1 : 2 : 3], or



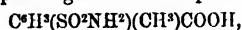
crystallises from alcohol in rosettes of needles or in thicker crystals, from water in flat flexible needles, and melts at 95° – 96° .

Paraxylenesulphamide, $C^6H^4.SO^2NH^2.H.CH^3.H^2$, melts at 148° ; *orthoxylenesulphamide*, $C^6H^4.CH^3.H.SO^2NH^2.H^2$, at 144° .

The constitution of the *metaxylenesulphamides* and the corresponding sulphonic acids is established by the following transformations: (1) The potassium salt of α -*metaxylenesulphonic acid* is converted by fusion with potassium cyanide into the nitril of xylic acid, $C^6H^4(CN)(CH^3)(CN)$. (2) The same potassium salt heated with sodium formate is converted into the corresponding xylic acid. (3) The same potassium salt fused with potassium hydroxide yields hydroxytoluic acid, melting at 151° and convertible into paracresol (p. 2024). (4) The sulphonic acid or the amide is converted by oxidation into α -hydroxyisophthalic acid,

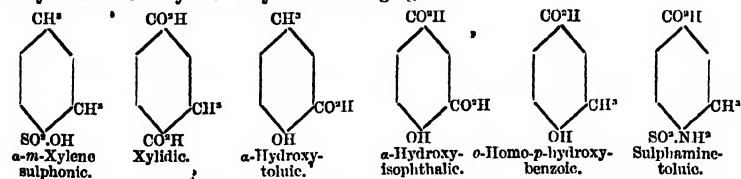


(p. 1532). (5) The *methylic ether* of liquid *xylenol* (p. 1541) is oxidised by potassium permanganate to methyl- α -hydroxyisophthalic acid. (6) The α -*amide* is oxidised by chromic acid or permanganate to a sulphaminetoluic acid,



which melts at 254° (corr.) and crystallises from hot water in long brittle anhydrous needles, sparingly soluble in cold water, also in alcohol and ether. By gentle fusion with potassium hydroxide it is converted into *o*-homo-*p*-hydroxybenzoic acid, $[CO^2H : CH^3 : OH = 1 : 3 : 4]$. (7) The *sulphamine-toluic acid* is oxidised by potassium permanganate to a sulphamine-isophthalic acid, convertible into α -hydroxyisophthalic acid.

The relations between these several products and α -*metaxylenesulphonic acid* may be more clearly shown by the following figures:



β -*Xylenesulphamide* (m. p. 95° – 96°) is oxidised by chromic acid to a sulphaminetoluic acid, melting at 202° – 205° , and convertible into a hydroxytoluic acid, which melts at 156° – 160° and is probably identical with Schotten's *ortho-homosali-*

cyclic acid (p. 2024). By oxidation with potassium permanganate, the β -amide is converted into a sulphamine-toluic acid, which may be separated from the acid solution by agitation with ether, and does not form a sparingly soluble acid potassium salt. The corresponding hydroxyisophthalic acid melts between 240° and 243° , and produces a cherry-red coloration with ferric chloride.

A mixture of equal parts of α - and β -xylenesulphamide melts at 110° ; a mixture of 2 parts α - and 1 part β -sulphamide at 122° – 123° (Jacobsen).

XYLENESULPHONIC ACIDS, $C^6H^4.SO^2H = C^6H^4(CH^3)_2(SO^2H)$ (Jacobsen, *Ber.* xi. 17). When metaxylene is dissolved in fuming sulphuric acid, the only products formed are the sulphonic acids whose amides melt at 95° – 96° and 137° (p. 2147); the same result was obtained with a metaxylene prepared from these amides.

α -Metaxylenesulphonic acid, [1 : 3 : 4], or $C^6H^3.H.CH^3.SO^2H.H^2$, best prepared by heating the corresponding amide (m. p. 137°) with strong sulphuric acid at 145° – 150° , crystallises in large laminae or flat prisms containing 2 mol. H^2O . Its barium salt forms small rhombic laminae or radio-crystalline groups of peculiarly-shaped lenticular bodies. The sodium salt crystallises from water in small scales, from alcohol in silvery laminae. The zinc salt, $(C^6H^3SO^2)^2Zn + 9H^2O$, is easily soluble and crystallises in stellate groups of needles or long rhombic prisms. The copper salt contains 6 mol. water.

The chloride, $C^6H^3SO^2Cl$, forms a radio-crystalline mass or prismatic crystals, melting at 34° . The sulphinic acid, $C^6H^3.SO^2H$, formed by reduction of the chloride, is also a crystalline mass, melting a little above 50° .

Potassium α -xylenesulphonate fused with sodium formate is converted into the potassium salt of xylic or xylylic acid, $C^6H^3(CH^3)_2.COOK$ (v. 1062); and by heating with potassium cyanide into the nitril of the same acid, $C^6H^3(CH^3)_2CN$.

β -Metaxylenesulphonic acid [1 : 2 : 3], or $C^6H^3.SO^2H.CH^3.H^2$, prepared from the sulphamide melting at 95° – 96° , has not been obtained in the crystalline state. Its barium and potassium salts are anhydrous, the former crystallising in stellate groups of microscopic needles, the latter in silky scales. The hydrated copper salt forms light-blue needles. The chloride is an oily liquid. The dimethylbenzoic acid, $C^6H^4(CH^3)_2.COOH$, formed from this sulphonic acid, crystallises in short needles melting at 97° – 99° , and when distilled with excess of lime yields metaxylene.

Bromo-metaxylenesulphonic Acids.—When the barium salt of α -metaxylenesulphonic acid is treated with an equivalent quantity of bromine, barium monobrom- α -m-xylenesulphonate is obtained in delicate scales containing 1 mol. water. The corresponding sodium salt, $C^6H^2Br(CH^3)_2SO^2Na + H^2O$, is easily soluble and crystallises in warty groups of needles. The analogously constituted ammonium salt forms silky tufts. The zinc salt $[C^6H^2Br(CH^3)_2SO^2]^2Zn + 9H^2O$, crystallises in long rhombic prisms; the copper salt in easily soluble greenish-white scales, containing 7 mol. water. The chloride forms large limpid prisms melting at 61° , slightly soluble in alcohol, insoluble in water. The amide crystallises in thick rhombic prisms, melting at 194° , easily soluble in ether, sparingly in cold water.

When m -xylenesulphonic acid in concentrated aqueous solution is treated with bromine, sulphuric acid and tribromoxylene are produced; the sodium salt treated in like manner yields the brominated acid, together with dibromoxylene.

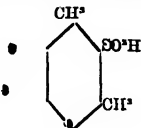
Monobromoxylene (b. p. 205° – 208°), treated with fuming sulphuric acid, forms monobrom- α -m-xylenesulphonic acid, $C^6H^2Br(CH^3)_2SO^2H + 2H^2O$, which crystallises in colourless laminae or prisms, and yields derivatives identical with those above described. This brominated acid dissolves easily in water, sparingly in sulphuric acid. Its constitution is represented by the formula [1 : 3 : 4 : 6], or $C^6.CH^2.H.CH^3.SO^2H.H.Br$ (R. Weinberg, *Ber.* xi. 1062).

Dibromo-m-xylenesulphonic Acid, $C^6HBr^2(CH^3)_2SO^2H$.—Jacobsen and Weinberg (*Ber.* xi. 1534) have obtained this acid by dissolving dibromo- m -xylene in fuming sulphuric acid at the temperature of 70° – 80° . It forms small anhydrous scales, having a silky lustre, slightly soluble in cold water, melting at 166° . Its barium salt is anhydrous, slightly soluble in water, and is deposited in indistinctly crystalline crusts. The sodium salt, $C^6HBr^2(CH^3)_2SO^2Na + 2H^2O$, forms nacreous laminae, slightly soluble in cold water. The chloride crystallises in colourless rhombic laminae melting at 107° ; the amide in felted needles, insoluble in alcohol, melting at 220° , decomposing at 230° .

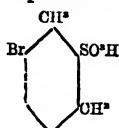
The dibrominated acid when treated with sodium-amalgam is converted into β -metaxylenesulphonic acid melting at 96° , and the amide dissolved in alcohol is converted by similar treatment, continued for a week, into a monobromo- m -xylene-

sulphonic acid, which crystallises in long needles, often grouped in asbestiform masses, melting at 161°.

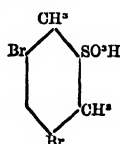
From these results and those of Weinberg (p. 2148) the following constitutional formulæ may be deduced for the compounds above described:



β -Metaxylene-sulphonic acid.



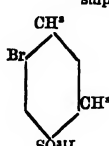
Monobrom- β -m-xylene-sulphonic acid.



Dibrom- β -m-xylene-sulphonic acid.



α -Metaxylene-sulphonic acid.



Monobrom- α -m-xylene-sulphonic acid.

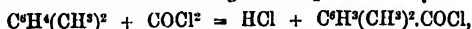
Paraxylenesulphonic Acid, $\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot 2\text{H}_2\text{O}$, forms a broadly laminar crystalline mass, or long flat prisms. From the product of the action of sulphuric acid on crude xylene, it crystallises before the ortho- and meta-acids, and may therefore be utilised for the preparation of paraxylene. Its *potassium salt* crystallises in flat silky needles containing 1 mol. water. The *sodium salt*, $\text{C}_6\text{H}_4\text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$, crystallises in flat longitudinally striated prisms of considerable size. The *barium salt*, $(\text{C}_6\text{H}_4\text{SO}_3)_2\text{Ba}$, forms either small shining crystalline scales or warty groups of thick crystals. 100 pts. water dissolve 2.27 pts. of this salt, at 0°, and 5.53 pts. at 100°. The *copper salt* crystallises in large light-blue tetelinic prisms with $8\text{H}_2\text{O}$; the *zinc salt* in long slender efflorescent needles containing $10\text{H}_2\text{O}$. The *chloride* crystallises in large flat prisms melting at 24°–26°; the *amide* in long needles melting at 147°–148°. The corresponding *sulphonic acid* dissolves readily in ether and alcohol, less readily in water, and crystallises in tufts of needles melting at 84°–88° (Jacobsen).

Orthoxylenesulphonic Acid, $\text{C}_6\text{H}_4\text{CH}_3\text{H.SO}_3\text{H.H}_2\text{O}$, is the only sulphonic acid formed on dissolving orthoxylylene in sulphuric acid. It crystallises more readily than either of its isomerides, in long rectangular tables, or thick flat prisms with roof-shaped summits. Its *barium salt*, $(\text{C}_6\text{H}_4\text{CH}_3)_2\text{Ba} \cdot \text{H}_2\text{O}$, which may be prepared by triturating the corresponding sulphinate with barium peroxide, crystallises in large nacreous laminæ, of which 100 pts. water dissolve 5.8 pts. at 0° and 33.6 pts. at 100°. The *sodium salt*, $\text{C}_6\text{H}_4\text{CH}_3\text{SO}_3\text{Na} \cdot 5\text{H}_2\text{O}$, crystallises in flat prisms. The *chloride*, $\text{C}_6\text{H}_4\text{CH}_3\text{SO}_2\text{Cl}$, separates from ethereal solution in prismatic crystals, melting at 51°–52°; the *amide*, $\text{C}_6\text{H}_4\text{CH}_3\text{SO}_2\text{NH}_2$, also in large prismatic crystals melting at 144°.

Orthoxylenesulphonic Acid, $\text{C}_6\text{H}_4\text{CH}_3\text{H.SO}_3\text{H.H}_2\text{O}$, prepared by the action of zinc-dust on the chloride (see SULPHONIC ACIDS, p. 1851), crystallises in large, thin, silky laminæ melting at 83° (Jacobsen, *Ber.* x. 1009).

XYLENOLS, $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OH}$, and **XYLENOLSULPHONIC ACIDS**, $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{OH}).\text{SO}_3\text{H}$. See PHENOL, HOMOLOGUES OF (p. 1540).

XYLIC or XYLIC ACID, $\text{C}_6\text{H}^1\text{O}^2 = \text{C}_6\text{H}^1(\text{CO}^2\text{H})(\text{CH}^3)^2$. This acid is most readily prepared by passing carbonyl chloride into metaxylene in presence of an excess of aluminium chloride, and occasionally heating the mixture to 100°, whereby xylic chloride is formed according to the equation:



and decomposing this chloride with water (Ador & Rilliet, *Ber.* xii. 1968). Its *potassium salt* is formed by heating potassium *m*-xylenesulphonate, [1 : 3 : 4] (p. 2148), with sodium formate (Picard, *Ber.* xi. 2120).

The acid prepared as above crystallises in large monoclinic prisms, melts at 126°, and boils at 267° (Ador & Rilliet, *Comp.* v. 1062).

Ammonium Xylate is very soluble in water, and may be obtained from the aqueous solution by spontaneous evaporation in small prismatic crystals, but decomposes when dried over the water-bath. The *barium salt*, $(\text{C}_6\text{H}^1\text{O}^2)_2\text{Ba}$, crystallises from a very strong solution in hard laminæ, and begins to decompose at 160°. The *calcium*

salt crystallises in transparent monoclinic prisms, which dissolve very slowly in water. The silver salt is but very slightly soluble in water even at the boiling heat, somewhat more soluble in boiling absolute alcohol, from which (and from hot water) it separates on cooling in tufts of microscopic needles.

Xylic Chloride, $C^6H^3(CH^3)^2.COCl$, prepared as above described, or by treating the acid with phosphorus pentachloride, is a colourless liquid, which boils at 235° , and crystallises on cooling in needles melting at 25° .

Xylamide, $C^6H^3(CH^3)^2.CONH^2$, prepared by treating the chloride with ammonium carbonate, is almost insoluble in cold water, and separates from the hot solution in needles (m. p. 181°), which are very soluble in alcohol. After sublimation it melts at 179° . This amide is a very stable body, not being decomposed by soda even on boiling; it is, however, readily acted on by hydrochloric acid, with reproduction of xylic acid. It dissolves in acids, forming somewhat unstable salts. The *anilide*, obtained by adding the chloride gradually to aniline, consists of crystals (m. p. 138), which are but sparingly soluble even in hot water, more easily in alcohol. On boiling with hydrochloric acid, it is partially decomposed (Ador a. Rilliet).

Xylonitril, $C^6H^3(CH^3)^2.CN$, obtained by heating potassium xylate with potassium cyanide, melts at 125° – 126° (Jacobsen, *Ber.* xi. 17).

An acid having the composition of xylic acid is formed (according to Picard, *Ber.* xi. 2120), together with other products, by heating the barium salt of cantharic acid, an isomeric of cantharidin (p. 276), formed by digesting that substance with hydriodic acid at 100° in a sealed tube. The acid thus produced melts at 140° , and is therefore different both from xylic and from paraxylic acid, the former of which melts at 126° , the latter at 163° (vi. 1130).

Appendix to Xylic Acid.

Mesitylenic Acid, $C^6H^3(CO^2H)(CH^3)^2$. The bromo-, nitro-, and amido-derivatives of this acid—the symmetrical modification of the acid $C^6H^{10}O_2$ —have been examined by H. J. Schmitz (*Liebig's Annalen*, cxci. 160; *Ber.* xi. 1828).

Bromomesitylenic Acids, $C^6H^2Br(CH^3)^2.CO^2H$. Two of these, α and β , are formed by direct bromination of mesitylenic acid, and are separated by the different solubilities of their barium salts.

The α -acid is formed, together with a smaller quantity of the β -acid, by digesting mesitylenic acid with 1 mol. bromine for 36 hours at ordinary temperature; also from the corresponding amido-acid, by converting this compound into the diazoperbromide, and gently heating the latter with absolute alcohol. It dissolves with great difficulty in cold, but readily in hot water, and crystallises therefrom by slow cooling in slender needles an inch long. It dissolves easily in alcohol, especially when hot, and separates therefrom in large colourless orthorhombic crystals. $a : b : c = 0.9274 : 1 : 0.4695$. Observed faces, ∞P^2 , ∞P^∞ , ∞P^∞ , P . Angle $\infty P^\infty : P = 65^\circ 21'$; $\infty P^\infty : P = 67^\circ 17'$. It melts at 146° – 147° , resolidifies at 131° , and if again heated melts at 137° – 138° . The α -barium salt, $(C^6H^2BrO^2)^2Ba + 4H^2O$, forms large colourless monoclinic crystals, moderately soluble both in hot and in cold water. $a : b : c = 3.0683 : 1 : 0.8040$; $\beta = 63^\circ 24'$. The calcium salt, $(C^6H^2BrO^2)^2Ca + 2H^2O$, separates from hot aqueous solution in very small slender needles, easily soluble in water.

β -Bromomesitylenic Acid, identical with that which Fittig and Storer obtained by oxidation of bromomesitylene (*Liebig's Annalen*, cxlvii. 1), is easily prepared from the corresponding amido-acid by the diazo-perbromide reaction. It is nearly insoluble in cold, very slightly soluble in hot water, from which it separates in compact monoclinic crystals; $a : b : c = 1.1932 : 1 : 0.7599$; $\beta = 70^\circ 35'$. Observed forms, $0P$, ∞P , P^∞ , ∞P^∞ . Angle, $\infty P : \infty P = 96^\circ 53'$; $0P : \infty P = 77^\circ 34'$; $P^\infty : 0P = 35^\circ 41'$. Cleavage parallel to P^∞ . The acid melts at 212° – 214° . The β -barium salt, $(C^6H^2BrO^2)^2Ba$, crystallises from hot water in colourless, slender, anhydrous needles.

Nitromesitylenic Acids, $C^6H^3(NO^2)(CH^3)^2$. The action of nitric acid on mesitylenic acid gives rise to two nitro-derivatives, one of which gives a sparingly soluble barium salt crystallising in tables, the other an easily soluble barium salt crystallising in needles.

α -Nitromesitylenic Acid, $C^6H^3(NO^2)(CH^3)^2.CO^2H$, is the acid obtained from the easily soluble barium salt, and is produced in larger quantity than the β -acid. It crystallises from water in splendid needles, melting at 210° – 212° , very difficultly soluble in cold water. From alcohol or ether it separates in large triclinic prisms. The α -barium salt, $(C^6H^3NO^2)^2Ba + 4H^2O$, crystallises in tufts of slender needles, which are

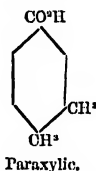
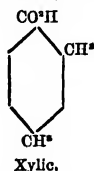
easily soluble in cold water, and dissolve in hot water in almost all proportions. The α -calcium salt is soluble in water in all proportions, and crystallises in long needles. The α -magnesium salt is also soluble in water in all proportions, and separates on evaporation in crystalline crusts. *Ethyl α -nitromesitylenate*, $C^6H^3(NO^2)O^2.C^2H^5$, crystallises in large tables, melting at 65° , insoluble in water, but easily soluble in alcohol.

β -Nitromesitylenic Acid, $C^6H^2(NO^2)(CH^3)^2.CO^2H$, is obtained from the difficultly soluble barium salt above referred to. It is insoluble in cold, and only very slightly soluble in hot water; easily soluble in hot alcohol, and separates on cooling in very large compact monoclinic crystals. This acid exhibits very characteristic properties on melting. When precipitated from the barium salt it melts at 175° , but when crystallised from alcohol it melts at 214° – 220° , and on cooling solidifies only at 162° , after which it fuses at 168° on re-heating. If a trace of alcohol be added to this fused acid, even when heated over 200° , it solidifies immediately, and begins to melt again only at 214° . The β -barium salt, $(C^6H^2NO^2)^2Ba + 4H^2O$, crystallises in monoclinic tables, sparingly soluble in cold, more readily in hot water. The β -calcium salt, $(C^6H^2NO^2)^2Ca + 6H^2O$, is sparingly soluble in hot water, and crystallises in long prismatic needles belonging to the monoclinic system.

Ethyl β -nitromesitylenate, $C^6H^2(NO^2)O^2.C^2H^5$, crystallises in long needles or thick prisms melting at 72° , insoluble in water, easily soluble in alcohol.

Amidomesitylenic Acids, $C^6H^3(NH^2)O^2$. The α -acid, prepared from the α -nitro-acid by reduction with tin and hydrochloric acid, crystallises from alcohol in long colourless needles melting at 186° – 187° . The β -acid, previously described by Fittig a. Brückner (vi. 823), melts at 235° .

XYLIDIC ACID, $C^8H^4O^4 = C^6H^2(CO^2H)(CH^3)^2(CO^2H)$. This bibasic acid is formed by oxidation of pseudocumene, $C^8H^2(CH^3)^3$ [1 : 2 : 4] (p. 1284), with dilute nitric acid or a warm solution of potassium permanganate, or by the action of nitric acid on xylic or paraxylic acid (vi. 1130): hence it has the constitution above indicated (Jacobsen, *Ber. x.* 855).



By the further action of potassium permanganate it is converted into trimellitic acid, $C^6H^2(CO^2H)^3$, which has therefore also the constitution 1 : 2 : 4 (G. Krinos, *Ber. x.* 1491).

Zinc Xylidate exhibits, more strikingly than any other known salt, the property of dissolving more abundantly in cold than in hot water, 100 pts. water at 0° dissolving nearly 30 pts. of it, at 100° only 0.735, and at 130° almost exactly 0.5 pt. The salt which separates at $+4^\circ$ from a solution saturated at -4° is anhydrous. At a little below -5° the entire liquid solidifies (Jacobsen, *Ber. x.* 859).

XYLIDINES, or AMIDOXYLENES, $C^8H^{11}N = C^6H^3(CH^3)^2.NH^2$. A. W. Hofmann (*Ber. ix.* 1292) has isolated, from the crude oils of high boiling point (200° – 240°) obtained in the manufacture of aniline, a xylidine which forms sparingly soluble salts with nitric and hydrochloric acids. This he calls provisionally α -xylidine, to distinguish it from an isomeride occurring together with it (β -xylidine), which forms a sparingly soluble nitrate, but an easily soluble hydrochloride. The two isomerides were separated by repeatedly crystallising from hot water the mixture of acetyl-compounds obtained by boiling them with glacial acetic acid; the α -compound, being the less soluble, was thus obtained pure.

α -Acetoxylidide forms large flat white needles, which melt at 127° – 128° and dissolve easily in alcohol. When boiled with strong hydrochloric acid, it is converted into xylidine hydrochloride. The base separated from this salt is an oil, colourless at first, but rapidly turning dark: its boiling point is 212° , and its sp. gr. 0.9184 at 25° . The *platinocchloride* has the formula $[C^8H^{11}(CH^3)^2.HCl]^2PtCl^4$.

A xylidine having the same properties as the foregoing is obtained by the action of methyl alcohol on toluidine hydrochloride at 300° .

The following derivatives of α -xylidine have been prepared:

Diszylthiocarbamide, $CS[NH.C^8H^3(CH^3)^2]^2$, was obtained by digesting xylidine

with carbon bisulphide till hydrogen sulphide ceased to be evolved. It is insoluble in water, and but sparingly soluble in boiling alcohol, from which it is deposited in dazzling-white hard crystals melting at 152° – 153° .

Xylol thiocyanate is formed by distilling the preceding compound with phosphoric anhydride. It is solid at ordinary temperatures, but melts very easily.

Diarylguanidine, $\text{CNH}[\text{NH} \cdot \text{C}^{\text{H}}(\text{CH}_3)^2]^2$, is readily formed by the action of lead oxide on xylolthiocarbamide in presence of alcoholic ammonia. It crystallises from hot alcohol in delicate white needles, which melt at 156° – 158° , apparently undergoing decomposition. It is insoluble in water.

Nitracetoxylicide, $\text{C}^{\text{H}}(\text{CH}_3)^2(\text{NO}^2)\text{NH}(\text{C}^{\text{H}}\text{O})$, formed by the action of strong nitric acid on acetoxylicide, crystallises from hot water or alcohol in yellow needles melting at 172° – 173° .

Nitroxylidine, $\text{C}^{\text{H}}(\text{CH}_3)^2(\text{NO}^2)\text{NH}^2$, is formed by boiling the last compound with strong hydrochloric acid till the liquid acquires a deep-red colour. It crystallises from hot water in fine orange-red needles melting at 69° , and dissolving sparingly in water, more freely in alcohol. It is but very slowly attacked by boiling soda-ley.

Xylene-diamine (Diamidoxylylene), $\text{C}^{\text{H}}(\text{CH}_3)^2(\text{NH}^2)^2$, is formed by the action of tin and hydrochloric acid on nitroxylidine. It forms glittering laminæ or delicate white needles, which melt at 74° – 75° . It is a faintly alkaline base, and forms crystallisable salts.

Wroblewsky (*Ber.* x. 1248) has obtained from nitracetoxylicide melting at 180° (probably identical with that above mentioned), by decomposition with strong sulphuric acid, a nitroxylidine melting at 76° ; from this a nitroxylene crystallising from alcohol in large flat needles, melting at 67° , boiling at 250° , and yielding by reduction a new xylidine, which remains liquid at 20° , has a sp. gr. of 0.9935, and boils at 220° – 221° (thermometer in the vapour). The hydrochloride of this xylidine crystallises in long colourless shining needles, the nitrate in long white needles having a nacreous lustre. The sulphate has the composition $(\text{C}^{\text{H}}\text{NH})^2\text{H}_2\text{SO}_4$. The acetyl derivative, $\text{C}^{\text{H}}\text{NH}(\text{C}^{\text{H}}\text{O})$, crystallises in needles melting at 144° .

Metaxylicidines (α and β) are formed by distilling α - and β -mesitylenic acid (p. 2150) with quick-lime. The α -metaxylicidine thus obtained is a colourless oil boiling at 212° (uncorr.) Its hydrochloride, $\text{C}^{\text{H}}(\text{NH}^2)\text{HCl}$, is slightly soluble in cold, more freely in hot water, and separates therefrom generally in large prismatic crystals (I.), but sometimes in tabular crystals (II.) According to measurements by Arzruni, the crystals I. belong to the monoclinic system. $a : b : c = 0.9178 : 1 : 0.2873$; $\beta = 85^{\circ} 46'$. Observed faces, ∞P , 0P , ∞R . Angle, $\infty\text{P} : \infty\text{R} = 47^{\circ} 32'$; $0\text{P} : \infty\text{R} = 74^{\circ} 1'$; $0\text{P} : \infty\text{P} = 76^{\circ} 2'$. The crystals are prismatically elongated in the direction of the axis c . The crystals II. are also monoclinic. $a : b : c = 0.9807 : 1 : 0.9531$; $\beta = 83^{\circ} 37.5'$. Observed faces, 0P , ∞P , ∞R . Angle, $\infty\text{P} : \infty\text{P} = 88^{\circ} 31'$; $0\text{P} : \infty\text{P} = 85^{\circ} 26.5'$; $0\text{P} : \infty\text{R} = 43^{\circ} 27'$. Tabular in the direction of c . The nitrate, $\text{C}^{\text{H}}(\text{NH}^2)\text{NHIO}^2$, forms prismatic crystals joined together so as to form large rhombic tables; it is sparingly soluble in cold, more freely in hot water. Acet- α -metaxylicide, $\text{C}^{\text{H}}\text{NH}(\text{C}^{\text{H}}\text{O})$, crystallises from alcohol in flat colourless needles melting at 127° .

β -Metaxylicidine is a colourless oil boiling constantly at 216° (mercury-column wholly in the vapour). The hydrochloride, $\text{C}^{\text{H}}(\text{NH}^2)\text{HCl}$, is readily soluble in water, and crystallises from hot water on cooling in large thin tables; by slow evaporation in colourless crystals, which, according to Arzruni, belong to the monoclinic system. $a : b : c = 0.5579 : 1 : 0.6175$; $\beta = 78^{\circ} 23'$. Observed faces, 0P (predominant), ∞P , ∞R . Angle, $\infty\text{P} : \infty\text{P} = 57^{\circ} 16'$; $\infty\text{P} : 0\text{P} = 79^{\circ} 39'$; $\infty\text{R} : \infty\text{P} = 58^{\circ} 50'$. The plane of the optic axes coincides with the plane of symmetry; an axis is visible at the edge through 0P (Schmitz, *Liebigs Annalen*, xciii. 160).

α -Metaxylicidine is, according to Schmitz, identical with Hofmann's α -xylidine, also with the xylidine which Wroblewsky obtained from metaxylene. This base, according to Wroblewsky, is converted, by substitution of methyl for the amido-group, into pseudocumene. Consequently α -metaxylicidine must be represented by the formula $\text{CH}^3 : \text{CH}^3 : \text{NH}^2 = 1 : 3 : 4$ or $\text{C}^{\text{H}}\text{CH}^3\text{H} \cdot \text{CH}^3\text{NH}^2\text{H}$, and β -metaxylicidine by $\text{CH}^3 : \text{NH}^2 : \text{CH}^3 = 1 : 2 : 3$ or $\text{C}^{\text{H}}\text{CH}^3\text{NH}^2\text{CH}^3\text{H}$. Corresponding formulæ likewise hold good for all the α - and β -derivatives of mesitylenic acid above described (pp. 2150, 2151).

Paraxylicidine, obtained by nitration of *p*-xylene and reduction of the nitro-compound with iron-filings and acetic acid, is an oily liquid which becomes yellow after a while, is moderately soluble in hot water, and boils at 220° – 221° . Its salts

crystallise well from acid solutions, but their neutral solutions decompose on boiling.

Paraxylylidine Sulphate, $[C^6H^{11}N]^2HSO_4$, crystallises in colourless plates. The **hydrochloride**, $C^6H^{11}N.HCl + H^2O$, forms large glistening plates, having a faint pink colour. It is more soluble than the sulphate. At 125° – 130° its water of crystallisation is expelled, and the anhydrous salt sublimes. The **nitrate**, $C^6H^{11}N.HNO_3$, forms pink needle-shaped crystals. The **oxalate** forms thick prisms having a pink colour. On heating to 125° – 130° , it splits up into water and **oxalparaxylylidide**, $[C^6H^9(CH^3)_2NH]^2C^2O^2$. This body is soluble in alcohol and in ether, and sublimes without melting at 126° , forming slender silky-white needles.

Acetoparaxylylidide (m. p. 138° – 139°) separates out as a crystalline mass on boiling paraxylylidine in glacial acetic acid. It is converted into **nitracetoparaxylylidide**, $[C^6H^9(CH^3)_2NO^2.NH.C^2H^3O]$, by the action of fuming nitric acid. This nitro-compound is a yellow crystalline powder melting at 192° (W. Schaumann, *Ber.* xi. 1537).

A chloroxylylidine of undetermined constitution is obtained, together with an oily xylylidine, by reducing mononitroxylene with tin and hydrochloric acid. It is a solid body, which dissolves with extraordinary facility in ether, alcohol, and benzene, is nearly insoluble in cold water, but dissolves in hot water, and crystallises therefrom in shining laminae melting at 92° – 93° . It volatilises readily with aqueous vapour.

Chloroxylylidine forms salts which crystallise well, but are stable only in strongly acid solutions. The **hydrochloride** crystallises with 2 mol. water, is fusible, sublimes without decomposition, and crystallises in crossed needles an inch long. The **sulphate** is but sparingly soluble in water, the **oxalate** still less soluble. The **acetate** and **nitrate** form tabular crystals (Jannasch, *Liebig's Annalen*, clxxvi. 55).

Xylydines with Chloral.—A compound having the formula $CCl^3.CH[NH.C^6H^9(CH^3)_2]^2$, analogous to those which chloral forms with other amines (vii. 311), is obtained by the action of chloral on xylylidine. It forms slender needles, easily soluble in ether, less soluble in alcohol, and melting at 95° – 99° . This melting point, which is low in comparison with those of the corresponding aniline and toluidine-compounds, seems to show that the xylylidine employed, which was prepared by separation as nitrate from aniline-tailings, was a mixture of several isomeric compounds (Wallach, *Liebig's Annalen*, clxxiii. 274).

XYLOQUINONE, $C^8H^6O^2$, formed by the oxidation of xylylene-diamine or of xylylidine, melts at 125° , and sublimes even at ordinary temperatures in golden-yellow needles. It bears a strong resemblance to its lower homologues, and is perhaps identical with the metaphlorone of Rommier a. Bouillon (iv. 496).

Xyloquinol, $C^8H^{10}O^2 = C^8H^2(CH^3)_2(OH)_2$, is prepared by treating the quinone with warm aqueous sulphurous acid, and separates from a hot aqueous solution in silvery plates melting at 212° . It is converted by oxidation into the quinone, and by the action of hydrochloric acid into monochlorxyloquinol (Nietzki, *Ber.* xiii. 473).

XYLYL KETONE, $C^{11}H^{18}O = C^8H^9.CO.C^3H^3$, is prepared by passing carbonyl chloride into xylene cooled to -15° , and gradually adding aluminium chloride. It remains liquid at -60° and boils at 340° . By saponification with potash it yields dimethyl-benzoic acid, convertible by oxidation into methylbenzene-dicarboxylic and benzene-tricarboxylic acids. By prolonged boiling it is resolved into water and the hydrocarbon, $C^{11}H^{18}$ (Ador a. Killiet, *Ber.* xi. 399).

Y

YAM. *Dioscorea edulis*. The tubers of this plant yield a milky juice containing a small quantity of fat, a resin having a slight and not bitter taste, and caoutchouc. In the north of Italy they are used for making brandy, and as food for men and cattle.

The tubers, somewhat shrivelled from loss of water, gave on analysis :

	Molat	Dried
Water	60.722	—
Ash, free from C, CO ² , and SiO ²	0.895	2.278
Protein compounds	4.485	11.419

	Moist	Dried
Extract with ether	0.348	
" alcohol and an alcoholic solu-	0.265	1.561
tion of carbon bisulphide		
Cane sugar	4.790	12.195
Levulose	0.180	0.458
Starch	25.185	64.121
Pectin and other non-nitrogenous extractive	2.033	5.176
matters		
Fibre	1.094	0.785
Sand	0.033	0.007

The pure ash gave :

K ² O	Na ² O	CaO	MgO	Fe ² O ³	P ² O ⁵	SO ³	SiO ²	Cl	
47.49	10.64	13.35	3.43	0.70	9.99	3.55	0.85	12.45	= 102.45
Deducting O equiv. to Cl									2.81
									99.64

(J. Moser, *Landw. Versuchs-Stationen*, xx. 113).

YEW. *Taxus baccata*. The green needles of this tree contain an alkaloid and other substances which have been examined by Amato n. Capparelli (*Gazz. chim. ital.* 1880, 340). The needles were exhausted successively with ether, alcohol, water, and dilute sulphuric acid. The extract left on evaporation of the ethereal solution was mixed with dilute sulphuric acid (1 : 20), and distilled in a current of steam, when an essential oil passed over, having an odour like that of wild fennel. The hot acid solution separated from the insoluble residue, deposited an amorphous powder on standing, and the filtrate from this, when treated with excess of baryta and agitated with ether, yielded the alkaloid. A colourless non-nitrogenous crystalline substance was extracted from the insoluble residue above mentioned by treating it with alcohol and small quantities of animal charcoal.

The alkaloid is a colourless, crystalline, nitrogenous substance, having a musty odour, sparingly soluble in water, easily in alcohol or ether. Dense white fumes are produced when a rod dipped in dilute hydrochloric acid is held near it. It gives a canary-yellow precipitate with phospho-molybdic acid, and with tannin a white precipitate which becomes crystalline on standing. Picric acid gives a yellow precipitate, and iodised potassium iodide reddish-brown crystals.

The non-nitrogenous crystalline substance forms stellate groups of needles, melting at 86°–87°, easily soluble in boiling alcohol, but only sparingly soluble in cold alcohol.

The solution obtained by treating the yew-needles with alcohol after they had been exhausted with ether was found to contain the same substances as the ethereal solution. From the aqueous and acid extracts, oxalic acid and small quantities of the alkaloid were obtained.

YTTRIUM. Atomic weight, 89.55 (yttria = Y²O³). See p. 736.

The probable existence of yttrium in the sun's atmosphere has been pointed out by C. A. Young (*Sill. Am. J.* [3], iv. 356), and by Lockyer (*Proc. Roy. Soc.* xxvii. 279).

An elaborate investigation of the spectra of yttrium, erbium, didymium, and lanthanum has been published by R. Thalén (*Bull. Soc. Chim.* [2], xxii. 350), one of the most important results of which is to show that the lines hitherto regarded as common to the spectra of these metals owe their existence to impurities.

On *Yttrium Salts*, see ERBIUM (p. 736). On the *Ferrocyanide*, see CYANIDES (p. 612). The chloroplatinate has the composition 2Y²Cl⁶.5PtCl⁴ + 51H²O; the chlorostannate, Y²Cl⁶.2SnCl⁴ + 16H²O (Cleve, *Bull. Soc. Chim.* [2], xxxi. 195).

METALS ALLIED TO YTTRIUM.

Erbium. At. w. 170.55. This element occurs as phosphate, together with didymium, in the Cornish mineral called *Rhabdophane* (p. 1756). Its probable existence in the sun has been pointed out by Lockyer. On the spectrum of Erbium Nitrate and of Erbia, see Lecoq de Boisbaudran (*Compt. rend.* lxxviii. 1167; lxxxix. 516; *Chem. Soc. J.* xxxvi. 862; xxxviii. 6).

From recent researches by Cleve it appears that the earth commonly called erbia is a mixture of three earths, viz. the true erbia, and two others which he designates as *holmia* and *thulia* (p. 2159).

Terbium. *Tr.* *At. w.* 98 or 147 (Delafontaine); 99 or 148.5 (Marignac), according as the oxide is regarded as TrO or as Tr_2O_3 .

The separate existence of this metal, originally pointed out by Mosander, but called in question by Buxen a. Bahr (v. 1064), and more recently by Cleve a. Hoeglund, has been established by the experiments of Delafontaine (*Ann. Ch. Phys.* [5], xiv. 238), and of Marignac (*ibid.* 247). Marignac prepares terbia from those portions of the mixed oxides obtained from gadolinite by Bahr a. Bunsen's process, which contain only traces of erbia. The oxides are dissolved in nitric acid, and subjected to a series of fractional precipitations with oxalic acid, the first portions of precipitate being the richest in terbia. By this treatment the whole of the yttria is separated, and the terbia is obtained mixed only with didymium oxide and erbia. The didymium is separated in the usual way by means of potassium sulphate; but for the separation of terbia from erbia no method has yet been discovered. According to Delafontaine, terbia is most advantageously prepared from samarskite, which contains but small quantities of yttria and erbia. The mixture of oxides obtained from this mineral is dissolved in nitric acid; the solution is treated with potassium sulphate to precipitate the cerium metals; and the syrupy solution of the remaining nitrates is mixed with a saturated solution of sodium sulphate, crystals of the same salt being added till no more is dissolved. A crystalline sulphate is thus obtained which, when treated with ammonium oxalate, yields an insoluble oxalate, leaving on ignition a dark yellow oxide, whereas the oxide obtained in like manner from the more soluble sulphate is of a much lighter yellow colour. The dark yellow oxide containing the greater part of the terbium is dissolved in a large excess of strong nitric acid, and a hot concentrated solution of oxalic acid is dropped into the liquid till a permanent precipitate is formed. After 24 hours the liquid is decanted, and subjected to fractional precipitation with oxalic acid, and this treatment is repeated a third, fourth, and fifth time. The united precipitates are then calcined and redissolved in nitric acid, and this solution is likewise subjected to a series of fractional precipitations with oxalic acid.

When the earths thus purified are dissolved by small quantities in dilute formic acid, and the clear solution is heated and slightly concentrated, a white pulverulent non-crystalline precipitate is obtained, yielding on ignition a base of deep orange-yellow colour, while the solution from which it has separated yields another base of somewhat lighter yellow colour; and on repeatedly dissolving the first of these bases in formic acid, and precipitating it therefrom by concentration till the percentage of base in the salt amounts to 60, a product is obtained consisting of pure terbia.

Terbia, after ignition at a moderate heat, has a deep orange-yellow colour, but becomes quite colourless when heated in a stream of hydrogen, or after very strong ignition. It dissolves slowly but completely in the most dilute acids; in hydrochloric acid with evolution of chlorine. Its solutions are colourless, and seem to possess no absorption-spectrum. The sulphate, $\text{Tr}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$, forms colourless crystals, isomorphous with the sulphates of yttrium, erbium, and didymium (Marignac).

Terbium Formate separates from solution on the sides of the vessels as a non-crystalline, closely-adhering crust; it burns without tumefaction when ignited, dissolves in about 30 parts of cold water, and appears to be not more soluble in hot water. The acetate crystallises in small coloured transparent prisms, less soluble than didymium acetate. It cannot be completely dried without decomposition, carbonises at a temperature below redness, and burns away slowly like starch (Delafontaine).

The sparing solubility of terbium formate, the colour of the oxide, and its property of forming an insoluble double salt with sodium sulphate, might lead to the conclusion that the supposed earth is nothing but a mixture of the oxides of lanthanum and didymium. But the formation of an oxalate in presence of an excess of strong nitric acid excludes the possibility of the presence of lanthanum, and the spectroscopic character of the base in question is altogether different from that of didymium. Lastly, the atomic weight of the metal, and the colourless character and solubility of the formate, acetate, and sulphate of terbium, preclude the possibility of the identity of terbia and erbia.

Philippium. *At. w.* between 90 and 95 for PpO , or 135 and 142.5 for Pp_2O_3 . The oxide of this metal has likewise been obtained from samarskite, but not quite pure, as portions of yttria and erbia adhere to it obstinately.

Philippium formate crystallises easily, either on cooling or by spontaneous evaporation, in small shining rhomboidal prisms, less soluble than yttrium formate, which is deposited in nodular groups from a syrupy solution; terbium formate is anhydrous and soluble in 30–35 parts of water. Sodio-terbic sulphate is scarcely soluble in water; the corresponding philippium-compound is easily soluble. Philippium oxalate is more soluble in nitric acid than terbium oxalate, but less soluble than the yttrium salt. Philippium nitrate becomes dark yellow when fused; yttrium and terbium

nitrates remain colourless. Philippium salts are colourless when pure; the oxide is decolorised by heating in a current of hydrogen, or simply by a strong heat, becoming yellow again on cooling in the air. Concentrated solutions of philippium salts give in the indigo-blue ($\lambda = 450$ nearly) a broad and very dark absorption-band, with its edges, more especially the right, very well defined; this band is not seen in yttrium, erbium, or terbium solutions. In the green there are two lines, one belonging to erbium, the other and less refrangible probably to philippium; finally, in the red there is at least one narrow band (Delafontaine, *Compt. rend.* lxxxvii. 559).

Phillipium appears also to occur in Sipylite (p. 1802), inasmuch as W. G. Brown (*Chem. News*, xxxviii. 269), in analysing that mineral, after separating the cerium metals from those of the yttrium-group, obtained with the solution of the latter an absorption spectrum, which exhibited bands agreeing very nearly with those observed by Delafontaine as characteristic of philippium.

Decipium. At. w. 106 for DpO , 159 for Dp^2O^3 . This metal, also discovered by Delafontaine (*Compt. rend.* lxxxvii. 632) in the samarskite of North Carolina, is intermediate in character between the metals of the cerium and yttrium groups. The oxide has not yet been sufficiently separated from that of didymium to exhibit its true colour. Its salts are colourless; the acetate crystallises easily, is less soluble than the didymium salt, but more so than the terbium salt; decipio-potassium sulphate is but slightly soluble in a saturated solution of potassium sulphate, but easily soluble in pure water.

Decipium nitrate gives in direct solar light an absorption-spectrum containing at least three bands in the blue and indigo. The most refrangible band is a little narrower than that of philippium or the band *m* of didymium; it is tolerably dark; its middle corresponds nearly with the wave-length 416, and is approximately in the middle of the space between Fraunhofer's lines G and H, but a little nearer to G. Neither didymium nor terbium gives bands in this part of the spectrum; the band characteristic of terbium is more to the right, and nearly out of the spectrum given by ordinary light. Under exceptional circumstances two well-defined bands, probably H and H₁, have been observed in the violet space beyond this band.

The second decipium band is narrower, darker, and less well-defined; it is situated in the less refrangible blue, and its middle corresponds with the wave-length 478; it is nearly in the same place as one of the didymium bands, but is much darker. Finally, more to the left, and nearer the limit of blue and green, there is an ill-defined minimum of transmission, which is possibly composed of two faint bands.

Samarium. Lecoq de Boisbaudran (*Compt. rend.* lxxxviii. 322; lxxxix. 212), in a spectroscopic examination of the unpurified earths from samarskite, observed an emission and an absorption spectrum, which showed lines and absorption-bands not belonging to any previously known element. The new element *samarium*, to which these lines belong, may be separated by repeated fractional precipitation from didymium and decipium. It is characterised by two blue bands, $\lambda = 480$ and $463\cdot5$, and probably by two others, 417 and $400\cdot75$.

Two other earths, distinguished as *yttria* α and β , have been obtained by Marignac (*Ann. Chim. Phys.* [5], xx. 535) from the mixture of those samarskite earths which, like erbia, ytterbia, &c., form nitrates not readily decomposed by heat. By taking advantage of the different solubilities of their double potassium sulphates in a saturated solution of potassium sulphate, these earths were separated into the four following groups:

I. *Double Sulphates, soluble in less than 100 times their volume of K^2SO_4 solution.* Molecular weight of oxide not less than 119 for MO or 357 for M^2O^3 . *Yttria* and *terbia*, with traces of the oxides of decipium and didymium, and probably traces of the oxide of $\text{Y}\alpha$ found in Group II. The *terbia*, even after strong ignition, had a faint chamæois tint, which disappeared on heating in a current of hydrogen, and reappeared when the oxide was again heated in the presence of air. These changes of colour were accompanied by very slight variations in weight.

II. *Double Sulphates, soluble in 100–200 vols. of K^2SO_4 solution.*—This portion consisted mainly of the oxide of the metal provisionally distinguished as $\text{Y}\alpha$. Molecular weight of oxide ($\text{Y}\alpha^2\text{O}^3$) about $361\cdot5$, being a maximum among those earths which most nearly approach it in their behaviour with potassium sulphate solution. This metal forms colourless salts. It is distinguished from all the metals of this class, except yttrium and ytterbium, by the very faint orange-yellow colour of its oxide, and by the fact that its salts show no absorption spectrum; from yttrium by the sparing solubility of its formate, and of its double potassium sulphate; from ytterbium by the much greater stability of its nitrate, and by the ease with which the ignited oxide dissolves in dilute acids.

III. *Double Sulphates, very slightly soluble in K²SO⁴ solution.* Mol. weight falls from 357 to 345 as the solubility decreases.—This group contains the oxide of Y α , a small quantity of the oxide of didymium which cannot be completely separated, and the oxide of a metal Y β , which forms a nitrate readily decomposed by heat, but is included in this group because its double potassium sulphate is very sparingly soluble in K²SO⁴ solution. The mol. w. of the oxide of Y β is probably somewhat lower than 346.8. Its sulphate forms small, short crystals similar to those of the sulphates of yttrium and didymium, but of a sulphur-yellow colour; they have the composition Y β (SO⁴)₂ • 8H²O.

Solutions of the salts of this base give a well-defined absorption spectrum which closely resembles that ascribed by Delafontaine to decipium, or, still more closely, that described by Boisbaudran as peculiar to samarium. Since these three bodies were obtained from samarskite by the same methods, it is probable that they are essentially one and the same substance. The mol. w. of the oxide of decipium is, however, according to Delafontaine, 390, whilst that of the oxide of Y β is below 346.8. Further, the salts of decipium are colourless, those of Y β have a yellow colour, the intensity of which increases the further the purification is carried. Probably either the substance obtained by Delafontaine was mixed with a considerable proportion of some other base having a high molecular weight, or that obtained by Marignac contained a base forming yellow salts, and having a much lower molecular weight. Further investigations are necessary to decide this point.

IV. *Double Sulphates, insoluble in K²SO⁴ solution.*—This group contained only didymium, which, however, could not be completely purified from traces of other metals.

The number of earths obtained from the samarskite of North Carolina now amounts to ten, viz. :—

	Colour	Mol. weight	Characteristic absorption-band
Yttria	White	Y ² O ³ = 227.1	None
Erbia	Rose	Er ² O ³ = 389.1	λ = 520–522
Terbia	Orange	Tr ² O ³ = 342	λ = about 400
Philippia	Yellow	Pp ² O ³ = 318	λ = about 449
Decipia	White (?)	Dp ² O ³ = 366	λ = about 416
Thoria	White	ThO ² = 263	None
Didymia	Brownish	Di ² O ³ = 338	λ = 372–377
Samaria	—	—	λ = 463.5 and 480
Y α	Faint orange-yellow	Y α ² O ³ = 361.5	No abs. spectrum
Y β	—	Y β ² O ³ = 346	{ Abs. sp. like those of decipia and samaria

J. L. Smith has obtained from the Samarskite of North Carolina an earth which he regards as peculiar, and designates as *Mosandria*. According to Marignac and Delafontaine, however, it is identical with terbia (*Compt. rend.* lxxxvii. 146, 281, 600; *Chem. Soc. J.* xxxvi. 12, 13, 117).

Ytterbium. At. w. 115 for YbO, 172.5 for Yb²O³. Matignac, in the course of his investigations on the gadolinite earths already noticed (p. 2155), obtained a small quantity of erbia, which subsequent experiments (*Compt. rend.* lxxxvii. 578) showed to be a mixture of two distinct oxides, viz. the true erbia and a new earth, which he calls *ytterbia*. This earth is colourless, and forms colourless salts; the nitrate is decomposed by heat without coloration.

Solutions of ytterbia give no absorption-bands, either in the ordinary spectrum or in the ultra-violet (Soret). The earth itself is less easily attacked by acids than the other earths of this family. It dissolves slowly in the cold, or at a gentle heat in slightly diluted acids; on boiling, it dissolves easily even in acetic and formic acids. *Ytterbium Sulphate* resembles, and is probably isomorphous with, the sulphates of yttrium and erbium; it dissolves easily and without residue in sulphate of potassium, no precipitate being formed even on boiling. A neutral and not too concentrated solution of *ytterbium chloride* is not precipitated by sodium thiosulphate; a very concentrated solution, containing erbium, gives a precipitate containing a larger proportion of erbium than is contained in the residual salts. Ytterbia precipitated by

potash, and submitted to a current of chlorine, dissolves completely in presence of excess of alkali.

The *formate* $C^3H^3YbO^6$ or $Yb^2O^3, 3C^2H^2O^3$ dissolves in less than its own weight of water, and crystallises in small crystalline nodules, resembling the formates of yttrium and erbium; it is decomposed with intumescence by heat, and loses its water of crystallisation at 100° .

The existence of this new earth in erbia throws doubts on the exactness of the equivalent of the latter, as determined by Bunsen and others, and would lead to the supposition that the molecular weight of erbia must be lower than that usually given.

Nilson (*Ber.* xii. 551) has also obtained ytterbia from gadolinite and from euxenite, and finds it to be a colourless, infusible earth of sp. gr. 9.175, insoluble in water, easily soluble in hot dilute acids, but attacked with difficulty, even by strong acids, in the cold. Its solutions have a sweet, astringent taste, are colourless, and give no absorption spectrum. The salts impart no colour to the Bunsen flame, but with the electric spark the chloride gives a brilliant spectrum. The *nitrate* forms large crystals, which melt in their water of crystallisation at 100° , and decompose when heated with evolution of nitric acid and nitrous fumes, and formation of insoluble basic nitrates. The *sulphate*, $Yb^2(SO^4)^3, 8H^2O$, forms large brilliant prisms which do not alter when exposed to the air, but lose their water at 100° . It dissolves slowly in boiling water, and is completely soluble in a saturated solution of potassium sulphate. The anhydrous sulphate may be heated to a high temperature without decomposition, but at a white heat it is completely converted into oxide. The *normal selenite* is obtained as a bulky amorphous precipitate by mixing solutions of sodium selenite and ytterbium sulphate. When treated with excess of selenious acid it yields an insoluble crystalline *acid selenite*, $Yb^2(SeO^3)^3, H^2SeO^3, 4H^2O$, which loses its water at 100° . The *oxalate*, $Yb^2(C^2O^4)^3, 10H^2O$, is formed as a bulky precipitate of small fine needles by the addition of oxalic acid to a solution of an ytterbium salt; this precipitate soon contracts, and assumes the form of short thick prisms. It loses $7H^2O$ at 100° , and is but slightly soluble in water and dilute acids.

That ytterbia is a sesquioxide is shown by the composition of the sulphate, analogous to and isomorphous with those of yttrium and didymium; by the composition of the acid selenite, and by that of the oxalate and formate, analogous respectively to the corresponding salts of didymium and yttrium; and, lastly, by the molecular heats and volumes of the oxide and the anhydrous sulphate.

Nilson finds the atomic weight of ytterbium to be somewhat higher than that given by Marignac, viz. 116 instead of 115, or 174 instead of 172.5.

Scandium. At. w. 44.03 (Nilson), 44.91 (Cleve), the metal being regarded as trivalent. This metal occurs only in gadolinite (0.002 to 0.003 per cent.) and yttritanite (0.005 per cent.) It was discovered by Nilson in 1879 (*Compt. rend.* lxxviii. 612; *Ber.* xii. 551), and further examined by Cleve (*Compt. rend.* lxxxix. 419) and by Nilson (*ibid.* xci. 118; *Ber.* xiii. 1439).

Scandia, Sc^2O^3 , may be separated from ytterbia by taking advantage of the fact that the nitrate decomposes more easily by heat than that of ytterbium, and that scandium sulphate produces in a saturated solution of potassium sulphate an insoluble double salt. This double salt nevertheless contains a little ytterbium sulphate, which may be finally removed by converting the two earths into nitrates, and submitting the latter to partial decomposition by heat; the ytterbium nitrate can then be washed out.

Scandia is a light, infusible, white powder resembling magnesia. It dissolves easily in boiling nitric and hydrochloric acids, but scarcely at all in the cold. It is not volatile, and gives no coloration to flame, although a very brilliant spectrum may be obtained from the chloride by the electric spark (Nilson).

The *hydrate* is a bulky white precipitate, drying up to semi-transparent fragments. It does not absorb carbonic acid from the air, is insoluble in ammonia and in potash, and does not decompose ammonium salts when heated with them (Cleve).

Scandium salts are colourless or white, and have an acid, astringent taste, very different from the sweet taste of the salts of the yttrium metals. The *sulphate* does not form distinct crystals; the *nitrate*, *oxalate*, *acetate*, and *formate*, are crystallisable. The *chloride* exhibits the following reactions: It gives no spectrum when heated in a gas flame. Potash and ammonia produce bulky white precipitates, insoluble in excess; tartaric acid prevents the precipitation by ammonia in the cold, but on heating an abundant precipitate falls. Sodium carbonate gives a precipitate, soluble in excess. Sulphuretted hydrogen produces no change; ammonium sulphide precipitates the hydrate. Sodium orthophosphate gives a gelatinous precipitate. Oxalic acid gives a curdy precipitate, quickly becoming crystalline; this precipitate dissolves in strong acids, and cannot be completely reprecipitated. Although apparently more soluble

than the oxalates of the other yttrium metals, it is found in the first precipitates in the fractional precipitation of a mixture of scandium and ytterbium by oxalic acid. Acid potassium oxalate precipitates a crystalline double salt. Sodium thiosulphate precipitates a boiling solution easily, but incompletely. Sodium acetate behaves similarly. The sulphates of potassium and sodium precipitate crystalline double salts, soluble in a saturated solution of the precipitant (Cleve).

The *nitrate* crystallises from a strong solution in small prisms; when strongly ignited, it is converted into oxide, but on treating this with water, a very basic nitrate generally dissolves, forming an opaque milky solution, which never becomes clear; this reaction is very characteristic of scandium. The *sulphate*, $\text{Sc}^2(\text{SO}_4)^3 + 6\text{H}_2\text{O}$, may be prepared as before mentioned; it is unalterable in the air, but loses 4 mols. of water at 100° , and the anhydrous salt is produced on gentle ignition; when strongly heated, it loses sulphuric acid and forms scandia. The *double sulphate*, $\text{K}^2\text{SO}_4 \cdot \text{Sc}^2(\text{SO}_4)^3 + x\text{H}_2\text{O}$, forms characteristic groups of small prisms. It is very slightly soluble in water, and quite insoluble in a saturated solution of potassium sulphate. The *selenite* and *oxalate* may be prepared by precipitation with the corresponding sodium salts; both are insoluble. The spectrum of scandium, as obtained by passing a powerful induction spark between aluminium poles moistened with a solution of the chloride, is very complicated, and contains more than a hundred lines. All the lines, which are very characteristic, are fine, with the exception of some in the yellow and orange, and seven strong lines in the blue-violet. A line at 4374 is slightly more refrangible than a prominent yttrium line, with which it might be confounded. Some very faint bands, situated at 5900–5730, are probably due to the oxide, as are possibly also the broad lines in the blue-violet at 6193–6016 (Thalén, *Compt. rend.* xci. 45).

Scandium agrees very closely in its atomic weight, and in the properties of its oxide and salts, with the element whose existence was predicted by Mendelejeff (*Liebig's Annalen, Supplementband*, viii. 133) under the name of *Ekaalor*, e.g. in forming a white oxide, M_2O_3 , infusible, soluble with difficulty in acids after ignition, insoluble in alkalis; also in forming colourless salts, and a sulphate which unites with potassium sulphate, yielding a double salt analogous in composition to common alum.

Thulium and Holmium (?). Cleve (*Compt. rend.* lxxxix. 478), in attempting to prepare pure ceria, has been led to the discovery of two other earths which he designates as *thulia* and *holmia*. On fractionating the mixture, and subjecting the several fractions to spectroscopical examination, it was found that, in addition to bands common to all the fractions, one band, $\lambda = 6840$, was strong in the residues rich in ytterbia, and wanting in those containing yttria and ceria, whilst two others, $\lambda = 6400$ and 5360, were strong in the yttria and ytterbia residues. The colour of the fraction treated for ytterbia was a violet-rose, whilst the yttria fraction had an orange tint.

The metal characterised by the first band, $\lambda = 6840$, Cleve proposes to name *thulium*; it would have an atomic weight of about 169.5 (the oxide being Tm_2O_3). Its oxide has a clear rose-colour. The other metal, *holmium*, is characterised by the bands $\lambda = 6400$ and 5360; it should have an atomic weight less than 162; its oxide seems to be yellow.

J. L. Soret (*Compt. rend.* lxxxix. 521) is of opinion that Cleve's holmium is identical with philippium, inasmuch as the bands $\lambda = 6400$ and 5360, which are said to be characteristic of it, are likewise found in the spectrum of philippium. Soret also claims to have observed Cleve's thulium ($\lambda = 6840$) in the portions of the gadolinite earths rich in ytterbium.

Z

ZEOLITES (v. 1066). The zeolites occurring in the basalt of the Limperichkopf, near Asbach, have been described by E. Weiss (*Jahrb. f. Min.* 1873, 1319). Among those occurring together in a cavity, philipsite (there of remarkable size) is the oldest, next follows natrolite, and lastly apophyllite.

Daubrée (*Compt. rend.* lxxx. 606) describes the recently formed zeolites from the spring of Bourbonne-les-Bains, Dep. Haute-Marne. Crystals of chabasite occur in small cavities in fragments of bricks, while those which are found imbedded in the mortar consist of lime-harmotome. C. Doelter (*Jahrb. f. Min.* 1875, 175) describes chabasite from the clefts in the monzonite of the Mal Inverno and of the Palle Rabbiosi, Monte Monzoni, and regards that of the latter locality as a secondary formation from anorthite.

See further GISMONDIN (p. 861): HEULANDITE (p. 1030); PHILLIPSITE (p. 1568).

ZEORA. The ethereal extracts of *Zeora sordida*, remaining after the usnic acid has crystallised out, contain two neutral crystallisable substances, zeorin and sordidin, which have been examined by Paternò (*Atti della Reale Accademia dei Lincei* [2], iii. [1876]; *Ber.* viii. 1359; x. 1382; *Gazz. chim. ital.* 1877, 281, 508). The separation and purification of these bodies is difficult, on account of the small proportion ($\frac{1}{4}$ per cent.) in which they occur in the lichen. The ethereal solution is evaporated down; the brown viscid residue is treated with cold alcohol, which removes a resinous substance; and the residue then left is boiled with a quantity of alcohol less than sufficient to dissolve the whole, so that nearly all the usnic acid present may remain undissolved. The alcoholic solution on cooling deposits the zeorin mixed with a small quantity of usnic acid, whilst the sordidin remains dissolved, and may be obtained by further concentration.

Zeorin, $C^{12}H^{22}O$, after purification by treatment with chloroform or boiling with potash-ley, which dissolves only the usnic acid, and crystallisation from ether-alcohol, forms very small but perfectly distinct pyramids with hexagonal base, colourless and transparent, and having a vitreous lustre. It melts at 230° – 231° , and volatilises without decomposition. It is but very slightly soluble in alcohol, ether, or chloroform, and quite insoluble in water. It is a neutral body, not attacked by alkalis. Nitric acid dissolves it, with omission of red fumes, and formation of a yellow substance insoluble in alcohol. It is but slightly attacked by dilute sulphuric acid. In composition and properties it is nearly allied to betulin.

Sordidin, $C^{12}H^{10}O^8$,* after repeated crystallisation from alcohol, forms colourless laminae or needles which melt at 210° , and volatilise without decomposition. It is insoluble in water, but dissolves readily in alcohol and benzene, sparingly in ether and in chloroform. By heating with aqueous potash, it is converted into a crystalline compound, which decomposes without fusion when heated above 250° . Zeorin is not decomposed by potash.

ZERECHTITE, see Tschuking (p. 2062).

ZINC. Atomic weight, 65. Occurrence in Plants and Animals.—Lechartier & Bollamy (*Compt. rend.* lxxxiv. 687) have found zinc in the human liver, in calf's liver, in beef, poultry-eggs, wheat, barley, maize, beans, and vetches.

Metallurgy.—On the roasting of zinc-ores, and the causes of the loss of zinc in the process, see Hasenclever (*Dingl. pol. J.* xcix. 284; cxvi. 165; *Jahresb. f. Chem.* 1871, 980; 1875, 1014). A blast-furnace for the smelting of zinc-ores is described by F. L. Clerc (*Dingl. pol. J.* cccxiv. 179; *Jahresb.* 1877, 1117).

Reactions.—Zinc immersed in an alcoholic solution of phosphorus, or in aqueous solutions of hydrogen phosphide, hydrogen sulphate, or iron salts, precipitates small quantities of phosphorus, sulphur, or iron on its surface, and retains them with great obstinacy. Zinc which has been kept in solutions containing phosphorus does not give up anything to water, alcohol, or ether, but carbon sulphide and chloroform dissolve phosphorus from it. It does not diminish in weight when heated at 140° in a stream of carbon dioxide, but it sustains some loss when agitated at ordinary temperatures with water and air. Zinc thus coated eliminates more hydrogen from dilute acids, &c. than unaltered zinc under conditions otherwise similar. Zinc may also be altered in like manner by solutions of hypophosphorous acid. The alteration appears to be due to surface attraction, not to chemical combination.

On the action of Zinc at high temperatures on mixtures of Hydrocarbons and Organic chlorides, see vii. 183, and p. 1063 of this volume.

Estimation.—C. Fahlberg (*Zeitschr. anal. Chem.* 1874, 379) describes a volumetric method of estimating zinc, depending upon the fact that this metal is completely precipitated from its solution in hydrochloric acid by potassium ferrocyanide, and that an excess of the normal solution is readily indicated by a solution of uranium. The accuracy of the method is not affected by the presence of manganese or aluminium, inasmuch as manganese ferrocyanide is soluble in potassium ferrocyanide, and aluminium solutions are not decomposed by that salt. The presence of nickel or cobalt is, however, injurious, since both these metals form insoluble ferrocyanides; but the quantity of them contained in zinc-ores is for the most part too small to have any sensible effect on the estimation. The ferrocyanide solution is made of such a strength that 1 c.c. of it will precipitate 0.01 g. zinc. It is titrated by means of pure zinc dissolved in hydrochloric acid, with addition of five times its weight of ammonium chloride. The zinc ferrocyanide readily falls out in thin flakes, and is free from alkaline ferrocyanide.

* Paternò originally assigned to sordidin the formula $C^{12}H^{11}O^7$; but subsequent experiments showed that the substance (m. p. 180°) whose analysis led to this formula was contaminated with zeorin.

The end of the reaction is determined by the brown colour produced on addition of a drop of uranium nitrate.

Ores containing galena or copper pyrites, besides blende, are treated with nitrohydrochloric acid, and the solution, after boiling with a little more hydrochloric acid, is saturated with sulphuretted hydrogen. The precipitated heavy metallic sulphides are filtered off; the iron in the solution is peroxidised with nitric acid; and the solution is allowed to cool before adding excess of ammonia. The iron is separated as ferric hydrate, and the solution now contains nearly the whole of the zinc. The precipitation is repeated till no more zinc is retained by the iron. The several ammoniacal solutions are neutralised with hydrochloric acid, 10 to 15 c.c. of acid of sp. gr. 1.12 being superadded, and the zinc is titrated with potassium ferrocyanide, regardless of the presence of manganese.

A similar method is described by F. W. Lyte (*Chem. News*. xxxi. 222; xxxvi. 89).

Zinc may also be estimated as *oxalate* in the same manner as manganese (Classen, p. 1264). The same reaction serves also to separate zinc from iron, which, in the state of ferric salt, is not precipitated by oxalic acid (p. 1104).

Compounds of Zinc.

On Alloys of Zinc and Copper, see COPPER (p. 566).

On the action of the 'Copper-zinc Couple' on various substances, see p. 1071.

Oxide, ZnO. Brügelmann (*Ann. Phys. Chem.* [2], lxxxvii. 1082) prepares this oxide in the crystalline state by heating zinc nitrate. It forms white or faintly yellowish, shining, hemimorphous pyramids belonging to the hexagonal system, and has a density of 5.782 at 215°. It is much less easily attacked by solvents than the amorphous oxide.

Zinc-dust.—The proportion of metallic zinc in the mixture of metal and oxide known by this name (vi. 1134) may be estimated by converting the hydrogen evolved by it into water by means of cupric oxide, and weighing the water (Fresenius, *Zeitschr. Anal. Chem.* 1878, 465).

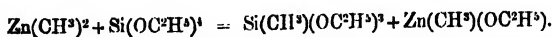
A cask of zinc-dust partly wet, which was being conveyed in a steamer, became red-hot and gave rise to a conflagration (*Dingl. pol. J.* cccxiv. 344).

Zinc Ferrite, ZnO, Fe₂O₃, is formed by precipitating a solution of ferrous chloride and zinc chloride with potash, and agitating the mixture with air till all the ferrous oxide is oxidised to ferric oxide; the precipitate dried and ignited exhibits magnetic properties.

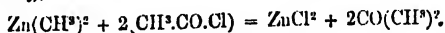
Zinc Phosphates and Arsenates (Demel, *Ber.* xii. 1171, 1279). **Primary Zinc phosphate**, ZnH₂(PO₄)₂ + 2H₂O, is obtained, by dissolving zinc oxide in phosphoric acid, and concentrating the solution, in large transparent triclinic crystals, which are not altered by alcohol or ether, but are decomposed by water, phosphoric acid passing into solution, and a white crystalline powder separating which has the composition 10ZnO, 4P₂O₅, 10H₂O, and is probably a mixture of several phosphates.

A solution of zinc oxide in *arsenic acid* evaporated to a syrupy consistence deposits after some time a crystalline crust composed of small plates, while the mother-liquor, on further concentration, yields an abundant crop of small white needles. Both these products, after washing with ether, consist of *secondary zinc arsenate*, ZnHAsO₄ + H₂O. This salt is decomposed by water, either hot or cold, giving up arsenic acid, and being converted into a crystalline salt having the composition 5ZnO, 2As₂O₃, 5H₂O, previously obtained by H. Salkowski (vi. 226). On adding an alkali to a solution of either of these salts in hydrochloric acid, a white bulky precipitate is formed, consisting of *normal or tertiary zinc arsenate*, Zn₃(AsO₄)₂ + 3H₂O, which Salkowski obtained by precipitating a solution of zinc sulphate with sodium arsenate.

Zinc-methyl, Zn(CH₃)₂. This compound, treated with *tetreylic silicate*, yields ethylic orthosilicoacetate together with zinc-methyl-ethoxyl or zinc methylethylate (p. 1793):



With *acetyl chloride* at low temperatures it forms acetone (Pawlow, *N. Petersb. Acad. Boll.* xxi. 497),



With *bromacetyl bromide* it yields methyl-isopropyl carbonol, see *PENTYL ALCOHOLS* (p. 1502).

Zinc-ethyl similarly treated appears to yield an octyl alcohol.

Zinc-ethyl treated with *sulphurous acid* yields ethylsulphurous, or ethylsulphinic acid, $C^2H^5 \cdot SO^2H$ (Zuckschwerdt, *Ber.* vii. 292).

ZINNWALDITE. A variety of lithia mica from Zinnwald in Bohemia (see *Mica*, p. 1320).

ZIRCON. A. E. Törnebohm (*Jahrb. f. Min.* 1877, 97) finds that zircon occurs as a widely diffused accessory constituent of Swedish felsite-porphry, curite, hellaflinta, gneiss, and especially in Swedish granites, and has also been found in the granites of Switzerland, Saxony, Tyrol, and North America.

G. A. König (*ibid.* 203, 944) has analysed zircons: (1). Occurring, together with needles of columbite, in the amazon-stone of Pike's Peak, Colorado, in crystals 6 mm. long, exhibiting the combination $P \infty P \infty$. (2). Crystals of the combination $P \cdot 0P \cdot \infty P$, imbedded in quartz or astrophyllite in El Paso county, Colorado:

	SiO ₂ .	ZrO ₂	Fe ² O ₃	MgO	H ² O	Sp. gr.
1.	28.00	50.00	—	8.93	3.47 = 100.40	4.065
2.	29.70	60.98	9.20	0.30	— = 100.18	4.538 at 12°

The analysis of the latter leads to the formula $Fe^2Zr^{10}Si^{10}O^{43}$.

F. Zirkel (*Jahrbuch f. Min.* 1876, 201) has detected zircon as a microscopic constituent in the granulites and mica-slates of Saxony, the gneisses and crystalline slates of North America, and the eclogites of the Fichtelgebirge. In these latter Sandberger found macroscopic zircon.

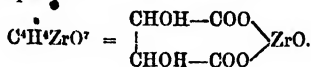
ZIRCONIUM. Atomic Weight, 90. Several compounds of this metal have been prepared and examined by S. R. Paykull (*Ber.* vi. 1467; xii. 1719), viz., the *tetrachloride*, the *chloride of zirconium and sodium*, $ZrCl_4 \cdot 2NaCl$, obtainable only in the dry way, *zircodiammonium chloride*, $ZrCl_4 \cdot 4NH_3 = Cl^2Zr \begin{smallmatrix} NH^2(NH^1)Cl \\ NH^2(NH^1)Cl \end{smallmatrix}$ analogous to platino-diammonium chloride (vii. 998), the *hydrated oxychlorides*, $ZrOCl_2 \cdot 8H^2O$, and $2ZrOCl_2 \cdot 13H^2O$, the latter, which is amorphous, being formed on dropping a solution of the chloride into hydrochloric acid; the *hydroxide*, $ZrO(OH)^2$, which in the moist state appears to absorb carbonic acid from the air; the *normal sulphate*, $Zr(SO^4)^2 \cdot 4H^2O$, and several crystallisable basic sulphates formed by combination of the normal salt with the hydroxide, e.g., $3ZrO^2 \cdot 4SO^3 + 15H^2O$, and $6ZrO^2 \cdot 7SO^3 + 19H^2O$, down to the formation of the *bibasic sulphate*, $ZrO^2 \cdot SO^3$, or $ZrO^2 \cdot Zr(SO^4)^2 + xH^2O$, which dries up to a gum. With potassium sulphate, several basic double salts have been obtained, e.g., $K^2SO^4 \cdot 2[ZrO^2 \cdot Zr(SO^4)^2] + 14H^2O$. The precipitate formed on boiling a solution of the mixed salts is also, as found by Berzelius, a highly basic double salt. The *arsenate*, $2(2ZrO^2 \cdot As^2O^3) + 5H^2O$, and a *phosphate*, $5ZrO^2 \cdot 4P^2O^5 + 12H^2O$, have also been obtained. The *normal oxalate* could not be prepared, but a *double oxalate*, $Zr^2C^2O^4 \cdot 2K^2C^2O^4 + 3H^2O$ or $4H^2O$, has been obtained.

Soluble basic zirconium-compounds have also been prepared by Endemann (*J. pr. Chem.* [2]. xi. 219). An alcoholic solution of zirconium *oxydichloride* prepared with the aid of heat yields, on addition of ether, an apparently crystalline precipitate, which,

after washing with anhydrous ether, has the composition $Zr^2O^3Cl^2$ or $\begin{smallmatrix} ClZr-O \\ || \\ ClZr-O \end{smallmatrix} O$.

It dissolves readily in water, and remains on evaporation at a gentle heat in the form of an amorphous powder. It is soluble also in cold alcohol, but is decomposed by warm alcohol. On adding ether to a solution of this compound prepared in the cold, a gummy precipitate is obtained, having the appearance of aluminium hydrate dried at a low temperature, and likewise soluble in water. It contains only $7HCl$ to $8ZrO^2$. Endemann regards these compounds as analogous to the hydrochloride of metastannic oxide, $SnCl^4 + 3SnO^2 = 2(SnOCl)^2O$, and to the compound $8HCl \cdot 9SnO^2$. An aqueous solution of *normal zirconium sulphate*, gave on addition of alcohol, a precipitate which contained only $6SO^3$ to $7ZrO^2$, and was soluble in water. The *basic sulphate* dissolves in a small quantity of water, but is instantly decomposed, on addition of a larger quantity of cold water, into a more basic salt which separates out and an acid salt which remains in solution. The salt precipitated by alcohol always retains alcohol, perhaps in the place of water of crystallisation. *Zirconium oxydichloride*, when repeatedly dissolved in water, and evaporated at a low temperature, continually gives off hydrochloric acid and becomes uncrystallisable.

Alkaline tartrates give with zirconium salts a white precipitate of zirconium tartrate having the composition



The solubility of this salt in caustic alkalis and alkaline tartrates indicates the existence of easily soluble double zirconium tartrates; and such salts are in fact obtained in crystalline form by heating the acid tartrates of potassium and sodium with zirconia. Their composition has, however, not yet been determined, as they are very much disposed to split up into salts of various composition (R. Hornberger, *Liebig's Annalen*, clxxxi. 232).

Cyanogen-compounds.—A solution of zirconium sulphate mixed with barium thiocyanate forms at first a colourless solution of *normal zirconium thiocyanate*, $\text{Zr}(\text{CNS})_4$; but this solution quickly decomposes, depositing a yellow body (probably pseudothiocyanogen), while the compound $\text{Zr}(\text{CNS})_2$ remains in solution.

Potassium ferrocyanide produces in zirconium solutions a yellowish-white precipitate, which soon turns greenish-blue, and forms when dry a powder having a fine blue colour with a greenish tinge, insoluble in water and decomposed by acids with evolution of hydrogen cyanide. Its composition is represented by the formula $(\text{Fe}^{2+})^{12}(\text{CN})^{12}(\text{Zr}^{4+})^3$, analogous to that of Turnbull's blue, $(\text{Fe}^{2+})^{12}(\text{CN})^{12}(\text{Fe}^{3+})^2$ (Hornberger).

ZÖBLITZITE. A hydrated magnesium silicate occurring at Zöblitz, at Kändler near Limbach (A), and as a coating on chrome iron ore in the serpentine of Hrubchitz, Moravia (B), also at Lettowich in Moravia:

SiO_2	Al_2O_3	Fe_2O_3	Mn_2O_3	H_2O	Sp. gr.
42.44	4.67	0.91	38.49	13.43 = 99.99	2.49 at 20°
42.57	9.12	1.82	32.90	13.19 = 99.60	—

Regarding the alumina as replacing part of the silica, these analyses lead to the proportions:

	SiO_2	Mg	H_2O
A	1	1.3	1
B	1	1.15	1

(A. Frenzel, *Jahrb. f. Min.* 1875, 680).

ZOISITE. This mineral, originally found on the Sau Alp and at Sterzing in Tyrol, at Fusch in Salzburg, and at Baireuth and Conradsreuth in Bavaria (v. 1085), occurs also in the island of Syra, in the corundum region of North Carolina, and in Delaware County, Pennsylvania.

Analyses. 1. From the glaucophane-bearing rocks of Syra (Lüdecke, *Zeitschr. Geol. Ges.* xxviii. 258, 262). 2. Dark rose-red to faintly reddish zoisite, occurring, together with green zeolites and green and yellow grossular, in friable grey quartz which forms a vein in the mica-slate gneiss of Leipersville, on the Crum Creek, Delaware County, Pennsylvania. Sp. gr. = 3.642 (G. A. König, *Zeitschr. Kryst.* ii. 302). 3. From the Cullakenee Mine, Clay County, North Carolina; greenish-white, formed from rose-red corundum. Sp. gr. 3.286 (König). 4. Greyish-white, formed from blue-grey corundum, which is still present in the nucleus; identical with the *unionite* of Smith a. Brush. Sp. gr. 3.224.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	K_2O	Na_2O	H_2O
1.	42.85	32.60	trace	—	—	21.37	0.21	—	—	95.55 = 99.58
2.	40.70	33.30	2.40	0.70	0.43	19.70	0.15	—	—	2.40 = 99.78
3.	40.70	33.86	0.81	—	—	24.05	0.22	not det.	—	0.63 = 100.27
4.	39.86	33.84	1.62	—	—	23.82	0.18	0.09	0.22	0.78 = 100.41

J. L. Smith (*Compt. rend.* lxxvii. 440) has published under the name of 'zoisite,' the analyses of two varieties, (A) light-green, (B) black, of a mineral which accompanies the corundum of North Carolina.

SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	CaO	MgO	Na_2O	H_2O
45.70	24.01	4.56	0.52	13.44	8.03	2.91	0.60
45.90	13.34	11.46	—	12.20	12.53	3.39	0.66

The proportion of silica is, however, rather large for an epidote or zoisite. The light-coloured variety has been described by Gemth (*Jahresb. f. Chem.* 1873, 1152) as *smaragdite*.

A D D E N D A.

ANTHRARUFIN, $C^{14}H^8O^4 = C^6H^3(OH).C^2O^2.C^6H^3(OH)$. (Schunck a. Roemer *Ber.* xi. 1176; Liebermann a. Böck, *ibid.* 1613). A dihydroxyanthraquinone formed in small quantity (2 p. c.) by the action of strong sulphuric acid on metahydroxybenzoic acid. It may be separated from anthraflavic acid and metabenzdihydroxyanthraquinone formed at the same time, by means of baryta-water, which dissolves those compounds, and purified by recrystallisation from glacial acetic acid.

Anthrarufin sublimes readily at 120° – 130° , and melts at 280° . It is nearly insoluble in water, and dissolves but sparingly in alcohol, forming a yellow solution from which it crystallises in yellow quadratic tables, exhibiting considerable iridescence. It dissolves sparingly also in glacial acetic acid, and crystallises therefrom in regular yellow saw-shaped crystals. The solution exhibits a faint green fluorescence. Anthrarufin dissolves to a considerable amount in benzene, less freely in ether and carbon sulphide. From chloroform it crystallises in prisms. These solutions produce no absorption-bands, but only a darkening of the spectrum.

A concentrated solution of anthrarufin in strong sulphuric acid exhibits a cherry-red colour by transmitted light and a strong scarlet fluorescence by reflected light. These colour reactions are extremely delicate. One part of anthrarufin in 1,000,000 pts. sulphuric acid, shows an evident carmine-red colour in strata 1 inch thick, while absorption-bands may be observed in solutions that appear colourless. Small quantities of nitric or nitrous acid change the carmine-red into a deep yellow which no longer exhibits any absorption-bands.

Anthrarufin dissolves in potash-solution with greenish-yellow colour; the addition of hydrochloric acid produces an orange-coloured precipitate, which when boiled with zinc-dust changes to a green fluorescent liquid. It is almost insoluble in sodium carbonate and in ammonia. Alcoholic lead acetate gives no precipitate in solutions of anthrarufin, but alcoholic copper acetate gives a brownish-red precipitate. Anthrarufin is not attacked by bleaching-powder, and does not produce lakes with alumina or oxide of iron. It yields a nitro-derivative.

Anthrarufin boiled with potash-solution gives, at a certain degree of concentration of the liquid, a brownish potassium-salt crystallising in needles; and on further evaporation an indigo-blue salt is obtained, which on addition of water is reconverted into the brown-red modification. Finally, if the mass be heated to fusion, a dark-blue lustrous mass is produced, which dissolves in water with a violet-blue colour; and on removing the unattacked anthrarufin and adding hydrochloric acid, a yellowish-brown substance is obtained which on sublimation yields small brown-red needles consisting of a trihydroxyanthraquinone or purpurin, $C^{14}H^8O^3$, which appears to differ from all the purpurins hitherto known; it dissolves with indigo-blue colour in potash, with violet colour in sulphuric acid.

Diacetyl-anthrarufin, $C^{14}H^8(C^2H^3O)^2O^4$, obtained by heating anthrarufin at 200° with glacial acetic acid, crystallises in yellow needles melting with decomposition at 245° (Schunck a. Roemer), at 244° (Liebermann a. Böck). It is quite insoluble in potash-ley, very slightly soluble in alcohol, more freely in glacial acetic acid; behaves with strong sulphuric acid like anthrarufin, and is reconverted into anthrarufin by boiling with potash.

HYDROXYETHYLANILINE, $C^8H^{11}NO = C^6H^4.NH(C^2H^3.OH)$. *Oxethyleno-aniline* (E. Demole, *Ber.* vi. 1024).—This compound is formed by adding aniline in molecular proportion to ethylene oxide in a well-cooled tube, then sealing the tube, exposing it for a few hours to a temperature of 50° , and fractioning the product till a portion is obtained boiling between 279° and 282° . It is a liquid colourless when recently prepared, very slightly soluble in water, alcohol, and ether, easily in chloroform. Its aqueous solution is coloured green by chloride of lime. When pure it boils at 280° .

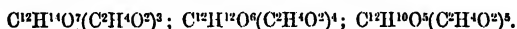
HYDROXYETHYL TOLUIDINE, $C^8H^{11}NO = C^8H^7.NH(C^2H^4OH)$. *Oxyethylene-toluidine* (Demole, *Ber.* vii. 635; *Liebig's Annalen*, clxxviii. 123).—This base is prepared by heating molecular proportions of ethylene oxide and paratoluidine at 100° in a sealed flask. The product, subjected to fractional distillation, yields a liquid which boils at 286° – 288° , and solidifies in dense tufts of white silky crystals melting at 37° , turning yellow on exposure to light, very soluble in alcohol, ether, chloroform, and benzene, soluble also in water. It is a strong base, yielding a deliquescent hydrochloride, and a platinochloride which forms brown not very regular crystals, and is not decomposed by boiling with water or alcohol—a character by which it is distinguished from the corresponding salt of hydroxyethylaniline. The *oxalate* forms small prismatic crystals or white tufts; the *acid sulphate* crystallises in colourless prisms.

Methylhydroxyethyltoluidine, obtained by heating molecular proportions of hydroxyethyltoluidine and methyl iodide in a sealed tube at 50° , is a fragrant uncrystallisable liquid; its platinochloride separates in tufts of red-brown very brittle crystals. By heating the monomethylated base with excess of methyl iodide at 100° , a liquid uncrystallisable iodide is obtained, which dissolves very readily in water and in alcohol, but is insoluble in ether. When treated with silver oxide it gives up its iodine, and is converted into a strong base, the platinum salt of which forms hard, ruby-coloured, highly lustrous crystals, having the composition of *dimethyl-tolyl-hydroxyethylammonium platinochloride*, $C^{12}H^{20}N^2O^2PtCl^2 = [(CH^3)^2(C^2H^4)(C^2H^4OH)NCl]^2PtCl^2$. With gold chloride very delicate tufts are obtained, having a splendid yellow colour.

Dihydroxyethyltoluidine, $C^{11}H^{12}NO^2 = C^8H^7.N(C^2H^4OH)^2$, is formed as a bye-product in the preparation of hydroxyethyltoluidine. It is a colourless, viscid, uncrystallisable liquid, boiling without decomposition at 338° – 340° ; turns brown somewhat quickly in contact with the air; is less soluble in alcohol than the monohydroxyethyl base. Its *platinum salt* is much more soluble in alcohol than that of the latter, and crystallises in shining ochre-yellow spangles.

INULIN, $C^{12}H^{20}O^{10}$. Lescœur & Morelle (*Compt. rend.* lxxxvii. 216) have prepared inulin from elecampane, dahlia, and chicory, and find, contrary to the statement of Ferrouillat and Savigny (*ibid.* lxxviii. 1571), that, from whatever source this substance is obtained, it is identical in chemical and physical properties.

Inulin prepared in the same manner from elecampane, dahlia, and chicory, gave with Laurent's polarimeter a rotatory power, $[\alpha]_D = -36.56, -36.57, -36.18$ respectively. Sodium inulate has a rotatory power $= -33^\circ$. Its acetic acid derivatives, obtained by the action of acetic anhydride, also correspond in character and composition; compounds have been obtained of the formulæ—



Inulin also plays the part of a weak acid, forming with alkalis compounds which are soluble in water, but are precipitated therefrom by alcohol. These compounds are amorphous, viscid, and translucent; they are unstable, as from their solution in water inulin is again precipitated on adding more water, or on passing carbon dioxide through the solution.

LACTIC ACIDS, ISOMERIC. Wislicenus, from experiments on the lactic acid obtained from flesh (sarcolactic acid), was led to regard it as a mixture of two acids, viz. *paralactic acid*, a dextrogyrate acid forming well-crystallised salts, and *ethylene-lactic acid*, the salts of which show but little tendency to crystallise. Erlennmeyer, on the other hand, failed to obtain an ethylene-lactic acid from sarcolactic acid, finding indeed in the mother-liquors of zinc paralaetate nothing but a small quantity of the zinc salt of ordinary lactic acid, together with a nitrogenous body. In another preparation of zinc sarcolactate made according to Liebig's directions (iii. 457) he found that the solution of that salt, crystallised to the last drop. Erlennmeyer also finds that ethylene-lactic acid, $CH^2OH.CH^2.COOH$, prepared by the action of hydrochloric acid or of caustic soda-ley on ethylene-cyanhydrin, $CH^2OH.CH^2.CN$, is absolutely identical with the so-called *hydracrylic acid* (vii. 717) obtained by the action of silver oxide on β -iodopropionic acid, $CH^2I.CH^2.COOH$. Wislicenus regarded the acids obtained by these two processes as isomeric, because he did not succeed in converting ethylene-lactic acid by the action of hydriodic acid into β -iodopropionic acid; but Erlennmeyer finds that the ethylene-lactic acid prepared from ethylene cyanhydrin is easily converted by this reaction into β -iodopropionic acid. It also yields the sparingly soluble zinc-calcium salt which is especially characteristic of *hydracrylic acid*.

It appears, then, that there are but two metameric modifications of lactic or hydroxypropionic acid, viz.:



The first of these is however susceptible of two isomeric modifications; one, the ordinary lactic acid of fermentation, being optically inactive, while the other (sarcolactic or paralactic acid), obtained from flesh, is dextrogyrate.

NORWEGIUM. A metal occurring, according to Tellef Dahl (*Ber.* 1679, xii. 1731), in a nickel-glance from the small island of Oterö. It is found as a black sulphide, together with copper, in the precipitate formed by hydrogen sulphide, and may be easily separated from copper by dissolving the precipitate in hydrochloric acid and mixing the slightly acid solution with a large quantity of water, whereupon the norwegium is precipitated as oxychloride. This metal is very similar to bismuth. Its specific gravity is 9.441, and atomic weight 145.95 for RO, or 218.93 for R^2O^3 ; melting point, 254°. Norwegium oxide, like bismuth oxide, is fusible and yields a metallic deposit before the blowpipe. The reactions of norwegium with potassium iodide, &c. are very much like those of bismuth. It is only in the reactions with alkalis and alkaline carbonates that any considerable difference between the two is to be observed, norwegium hydroxide being soluble in caustic potash and in a large excess of the carbonate of ammonium or sodium, whereas bismuth oxide is sparingly soluble or insoluble therein.

OZONE. *Liquefaction and Colour in the Gaseous State.*—When a gaseous mixture very rich in ozone, obtained by the action of electricity on oxygen at a very low temperature, was submitted to strong pressure at a temperature of -23° , an azure-blue colour appeared in the tube, and as the pressure increased, the colour deepened, until, when the gas was under a pressure of several atmospheres, the colour had become indigo-blue. On suddenly removing the pressure, a momentary white mist was observed in the tube, indicating a condensation to the liquid, or perhaps to the solid state. The blue colour is an essential character of ozone, and may be seen whenever a sufficient thickness of a mixture containing it is viewed. Thus the oxygen issuing from Berthelot's silent discharge apparatus exhibits a sky-blue colour when viewed through a column 1 meter long (Hautefeuille a. Chappuis, *Compt. rend.* xci. 522).

On the effect of Ozone on the Colour of the Atmosphere, see Hartley (*Chem. Soc. J.* 1880, xxxix. 113).

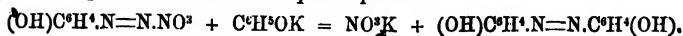
PHENOL-DIAZINS, or *Azophenols* (Weselsky a. Benedikt, *Wien. Akad. Ber.* [2 Abth.], lxxvii. 773; *Ber.* xi. 398).

Diphenol-diazins, $\text{C}^6\text{H}^4(\text{OH})\cdot\text{N}=\text{N}\cdot\text{C}^6\text{H}^4(\text{OH})$. The *ortho*- and *para*-compounds are formed by the action of melting potassium hydroxide on the corresponding nitrophenols. Metanitrophenol does not yield a diazin-compound. To prepare *o*-diphenol-diazin, 5 g. orthonitrophenol are added to a four- or five-fold amount of potassium hydroxide melted with a small quantity of water, and the mixture, which has at first a red colour, due to the presence of potassium-*o*-nitrophenol, becomes dark green with metallic lustre, and begins to froth up strongly and give off ammonia. The froth sinks rapidly, leaving a dark red melt, which is to be dissolved in water and supersaturated with dilute sulphuric acid; and the yellow-brown flocks thereby separated are freed from undecomposed nitrophenol by washing with water, then pulverised and exhausted with boiling ether. On leaving the ether to evaporate, the diphenol-diazin remains, and may be purified by crystallisation from alcohol.

Orthodiphenol-diazin is insoluble in water, dissolves in about 300 pts. cold alcohol, more freely in boiling alcohol, abundantly in ether, and crystallises from alcohol in anhydrous laminae having a golden lustre; it melts at 171° , and volatilises without decomposition, subliming in reddish-yellow needles. It dissolves in alkalis, forming reddish-yellow solutions from which it is precipitated unaltered by acids. Its *lead salt*, $\text{C}^{12}\text{H}^8\text{N}_2\text{O}^2\text{Pb}$, separates as a red anhydrous precipitate on mixing the alcoholic solution of lead acetate and *o*-diphenol-diazin. The *barium salt*, prepared by adding titrated solutions of caustic baryta to alcoholic solutions of the diphenol-diazin, crystallises after some time in wavelitic groups of needles having a splendid red colour. At 100° it gives off its water of crystallisation, and acquires a fine brown colour. *Tetrabrom-o-diphenol-diazin*, prepared like the corresponding *para*-compound (*infra*) by treating *o*-diphenol-diazin in ethereal solution with excess of bromine, crystallises in needles having a dark yellow colour and metallic lustre. When fused with potash it turns reddish-violet.

Para-diphenol-diazin is formed: 1. When *p*-nitrophenol in portions of 5 to 10 grams is added to a five-fold quantity of potassium hydroxide fused with a little water, and the mixture is heated till it ceases to froth, and assumes a brown-violet colour. On saturating it with dilute sulphuric acid, crude *p*-diphenol-diazin separates

in the form of a yellow scum, which is to be collected, dried, dissolved in ether, then freed by filtration from considerable quantities of gummy and carbonaceous substances, and the ether finally evaporated off. By repeated crystallisation from dilute alcohol, the *p*-diphenol-diazin is obtained in bent needles or compact grains having a red-brown colour and mostly a steel-blue reflex. The product amounts to 30 per cent. of the calculated quantity. For purification it is dissolved in dilute potash-ley, precipitated by carbonic acid, and recrystallised from dilute alcohol. 2. By the action of potassium-phenol on the nitrate of *p*-diazophenol:



To prepare it, the solutions of 10 g. diazophenol nitrate in 200 c.c. water and 7.22 g. potassium-phenol are mixed together, whereupon the liquid quickly turns dark red and begins to deposit a resin. On filtering the liquid after twenty-four hours, and adding dilute sulphuric acid, a copious dark red crystalline precipitate is formed which may be partly purified by washing with cold water and agitation with dilute solution of sodium carbonate. The paradiphenol-diazin then remains undissolved, and may be further purified by agitation with ether, which dissolves it, evaporating off the ether, and recrystallising the residue from alcohol with the aid of animal charcoal.

Paradiphenol-diazin is nearly insoluble in water, but dissolves readily in alcohol, ether, and benzene, and crystallises in light brown shining triclinic crystals, without metallic reflex. It melts at about 204° , and at the same temperature begins to decompose with strong intumescence. Its compounds with alkalis dissolve in water and in alcohol with splendid orange colour; it has not yet been separated from these solutions. The *barium salt*, $\text{C}^{12}\text{H}^4\text{N}^2\text{O}^2\text{Ba} + 4\text{H}_2\text{O}$, obtained by mixing an alcoholic solution of the diazin with the equivalent quantity of caustic baryta in aqueous solution, forms yellow crystalline granules which at 100° give off their water and turn brown-red. The *lead salt* may be prepared in a similar manner.

Tetrabromo-p-diphenol-diazin, $\text{C}^{12}\text{H}^4\text{Br}^4\text{N}^2\text{O}^2$, is obtained by treating the diphenol-diazin dissolved in 60 pts. of ether with an excess of bromine, as a granular substance which dissolves in benzene and crystallises therefrom in golden-yellow needles. It does not dissolve without decomposition in potash-ley, and when fused with excess of potassium hydroxide and a few drops of water, it yields a blue melt, which on exposure to the air becomes first violet and then red.

SILICON-ETHYL SERIES. Compounds containing a double atom of silicon, $\equiv\text{Si}-\text{Si}\equiv$, and therefore analogous to ethane and its derivatives, have been prepared by Friedel a. Ladenburg (*Ann. Chim. Phys.* [5], xix. 390). The starting-point for the preparation of these compounds is *silicon tri-iodide*, Si^2I^6 , which is prepared by heating silicon tetr iodide with finely divided silver (reduced by zinc from moist silver chloride), in sealed tubes at 290° - 300° for several hours. The contents of the tube are freed from unaltered tetriodide by repeated washing with small portions of dry carbon bisulphide; a larger quantity of hot carbon bisulphide is then added, and the mixture filtered as rapidly as possible out of contact with the moisture of the air. On cooling, the solution deposits small colourless hexagonal prisms of Si^2I^6 , which fume in moist air, and dissolve in potash with evolution of hydrogen. Silicon tri-iodide may be fused in a vacuum, but decomposes partially at 250° . It cannot be distilled at atmospheric pressure or in a vacuum, but on heating it, a portion sublimes, and the remainder decomposes into the tetriodide and an orange-coloured substance which appears to be SiI^2 .

Silicon tribromide, Si^2Br^6 , is obtained by adding an equivalent of bromine to a solution of the hexiodide in carbon bisulphide. It crystallises in rhombic plates, presenting the optical phenomena of biaxial crystals, and is therefore not isomorphous with the corresponding iodide.

Silicon trichloride, Si^2Cl^6 , is obtained by gently heating a mixture of silicon tri-iodide and mercuric chloride. The product is distilled off, rectified over mercuric chloride, and purified by fractional distillation. It is a colourless liquid, distilling between 144° and 148° , and crystallising at about -1° ; it fumes in the air, and is decomposed by water, with formation of a product which in great part dissolves in the acid liquid. All attempts to prepare this substance in the dry way by the action of silicon, silver, zinc, sodium, and hydrogen on silicon tetrachloride at a high temperature were unsuccessful. Troost a. Hautefeuille, however, have recently prepared Si^2Cl^6 by the action of silicon tetrachloride on fused silicon, at a temperature at which porcelain begins to soften.

Silico-oxalic hydroxide, $\text{H}^2\text{Si}^2\text{O}^4$.—When crystals of silicon tribromide are introduced into ice-water, hydrogen is evolved, and a white substance deposited which, after drying in a vacuum and then at 100° , has a composition expressed by the

formula $\text{H}^2\text{Si}^2\text{O}^4$. Treated with potash, it gives off hydrogen in theoretical proportion, and when burnt with oxygen or heated in the air, it decomposes with incandescence, leaving a residue of silica in the proportion required by the equation: $\text{H}^2\text{Si}^2\text{O}^4 + \text{O} = \text{H}^2\text{O} + 2\text{SiO}^2$. The air-dried substance contains 10.4 per cent. water, the formula $\text{H}^2\text{Si}^2\text{O}^4 + 2\text{H}^2\text{O}$ requiring 12.8 per cent. The formation of silico-oxalic hydroxide may be explained by supposing that $\text{Si}^2(\text{HO})^2$ is first produced, and then converted into $\text{Si}^2\text{O}^2(\text{HO})^2$ by the loss of $2\text{H}^2\text{O}$. Although this substance is the chemical analogue of oxalic acid, it has no acid functions; bases, even the most dilute, decompose it with evolution of hydrogen, just as oxalic acid under certain conditions is decomposed by potash. Silico-oxalic hydroxide may also be prepared by the action of silicon triiodide on absolute alcohol, the ethyl iodide, which is formed at the same time, being removed by distillation.

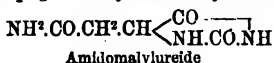
Silicon triethide, $\text{Si}^2(\text{C}^2\text{H}^3)^3$.—Silicon tri-iodide is added in small quantities to zinc-ethyl in the proportion of Si^2I^6 to $3\text{Zn}(\text{C}^2\text{H}^3)^2$. A brisk reaction ensues, and a white substance is deposited. The product is distilled, the distillate washed with water to remove zinc-ethyl, agitated with concentrated sulphuric acid (to remove a substance which appears to be the oxide of silicon-triethide, vii. 1083), again washed with water, dried, and submitted to fractional distillation. The distillate boiling at 150° – 154° is silicon tetraethide, that coming over between 250° and 253° is silicon triethide, $\text{Si}^2(\text{C}^2\text{H}^3)^3$. Silicon triethide is a limpid, slightly oily liquid, with a faint odour resembling that of silicon tetraethide. It burns with a bright flame, producing clouds of silica. Two vapour-density determinations, made at about 300° , gave the numbers 8.53 and 8.63, theory requiring 7.96. The excess was probably due to the presence of the above-mentioned oxide of silicon-triethide. The density of the liquid silicon triethide is 0.8510 at 0° , 0.8403 at 20° , compared with water at 0° and 20° respectively.

SUCCINIMIDE, $\text{C}^4\text{H}^3\text{NO}^2$ = $\begin{array}{c} \text{CH}^2.\text{CO} \\ | \\ \text{CH}^2.\text{CO} \end{array} \text{NH}$. This compound, treated with bromine, yields dibromosuccinimide, which crystallises in rhombic prisms melting at 225° , together with bromofummarimide, $\begin{array}{c} \text{CBr}.\text{CO} \\ | \\ \text{CH}.\text{CO} \end{array} \text{NH}$, melting at 150° – 152° , and another body, perhaps monobromosuccinimide, which melts at 105° – 120° (Kisielinski, *Wien. Acad. Ber.* [2 Abth.], lxxiv. 561).

SUCCINURAMIDE, $\text{C}^8\text{H}^8\text{N}^2\text{O}^4$, is obtained by evaporating the mixed solutions of potassium cyanate and asparagine:

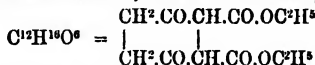


It forms colourless prismatic crystals, sparingly soluble in water, nearly insoluble in ether and in alcohol. It melts at 137° – 138° , decomposing at the same time, with formation of a midomallylureide, which when evaporated down with hydrochloric acid of sp. gr. 1.12, yields mallylureidic acid:



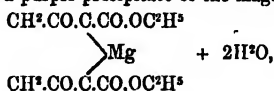
(Guareschi, *Gazz. Chim. ital.* 1877, 404).

SUCCINYL-SUCCINIC ACID, $\text{C}^8\text{H}^6\text{O}^6$. The diethylic ether of this acid,



which Fehling obtained by the action of potassium on diethylic succinate, regarding it however as $\text{C}^8\text{H}^6\text{O}^6$ (v. 43), has been further examined by F. Herrmann (*Ber.* vii. 1039). It is neutral, insoluble in water, but dissolves in alcohol, ether and benzene, forming solutions which exhibit a splendid light blue fluorescence, and separates in large light-yellowish triclinic crystals melting at 126° – 127° . On the crystalline form see Arzruni (*Zeitschr. Kryst.* i. 449).

Alcoholic potash added to its alcoholic solution throws down the *monopotassium compound*, $\text{C}^8\text{H}^4\text{K}^2\text{O}^6$, which, when treated with excess of potash, is converted into the *dipotassium-compound*, $\text{C}^8\text{H}^4\text{K}^4\text{O}^6$, which has a splendid orange colour, and forms a yellow solution in water. This solution is very unstable, but when recently prepared gives with magnesium salts a purple precipitate of the magnesium-compound

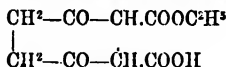


which gives off water and turns yellow at 80°, but recovers its original colour when drenched with water.

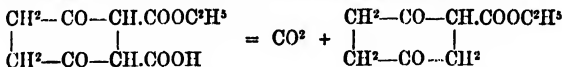
Ira Remsen (*Ber.* viii. 1408) has also obtained this magnesium compound, but not in the pure state, by boiling the ether, $C^{12}H^{16}O^4$, with magnesia. He describes this ether as crystallising in flat needles with a tinge of yellow, and melting at 128°. By adding an alcoholic solution of soda to a solution of the ether in alcohol, or by the action of sodium-amalgam on the latter, he obtained immediately a fine red bulky precipitate made up of microscopic needles, which, after washing and drying (whereupon it turned yellow), had the composition of the sodium-salt, $C^{12}H^{14}Na^2O^6 + 4H^2O$. This sodium-compound is very soluble in water, and hydrochloric acid added to the solution throws down the original ether. The barium compound, $C^{12}H^{14}BaO^6 + H^2O$, is obtained in like manner as a precipitate, having a fine rose-red colour, and turning yellow on drying. It is not decomposed by boiling with water or alcohol. With lime-water, the lemon-yellow calcium-compound, $C^{12}H^{14}CaO^6 + H^2O$, is obtained. The ether, $C^{12}H^{14}(C^2H^5)^2O^4$, is not attacked by acetylchloride, ammonia, or nascent hydrogen; it is very slowly oxidised by potassium permanganate and by nitric acid; decomposed by water at 150°. Remsen does not consider that the constitutional formula proposed by Wislicenus for the acid, $C^{12}H^{16}O^4$, is satisfactorily established.

Action of Alkalis on Diethylic Succinylsuccinate (Hermann, *Ber.* x. 107). The mode of action of alkalis on this ether varies accordingly as it takes place in presence or absence of air.

I. *In absence of air*.—1. When the yellow alkaline solution is left for two hours, the undecomposed ether then precipitated by carbon dioxide, and the filtered liquid acidified with acetic acid, there is thrown down a crystalline greenish-white powder, which is sparingly soluble in cold alcohol, ether, and cold water. Neutral solutions of this body are coloured deep violet by ferric chloride. It melts at 98°, evolving carbon dioxide, to a pale yellow liquid, which does not solidify, and is readily decomposed by boiling water, with copious evolution of carbon dioxide. According to analysis the substance is *monethylic succinylsuccinate*, having the formula—



This formula is supported by the facts that the substance yields alcohol when heated with potash, and that it gives off at 100° a quantity of carbon dioxide agreeing with the following equation, thus yielding *ethylic succinylpropionate* :—



The last product is an oily liquid of intensely bitter taste and faint odour, dissolving easily in alcohol and ether, and sparingly in cold water. Its solutions are coloured a pure violet by ferric chloride.

2. In the liquid filtered from monethylic succinylsuccinate, dilute sulphuric acid produces a yellowish-white, crystalline precipitate having an acid reaction, sparingly soluble in cold water, more freely in alcohol and ether. The solutions are coloured violet by ferric chloride. This substance is readily decomposed by boiling water, evolving carbon dioxide. It is regarded by Hermann as *succinylsuccinic acid*.

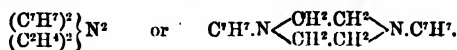
3. The liquid from which the preceding substances have been separated contains yet another decomposition-product, which has not been isolated.

II. *In presence of air* the decomposition described above is accompanied by absorption of oxygen, in consequence of which there is formed, besides the foregoing decomposition-products, an acid which crystallises from boiling water in pale yellow, hair-like needles. This body dissolves very easily in alcohol, ether, and boiling water, the solutions exhibiting a greenish fluorescence, and giving a deep blue colour with ferric chloride. When cautiously fused with potash and afterwards acidified with sulphuric acid, it evolves carbon dioxide, and yields quinol. From these reactions, and the numbers obtained by analysis, it is inferred that the substance is *quinol-dicarboxylic acid*, $C^6O^2H^4(COOH)^2$.

VINYL-TOLUIDINE, $C^9H^{11}N$, which Wurtz obtained by heating toluidine with ethylene chlorhydrin (vi. 1105), is also produced in small quantity by heating hydroxethylene-toluidine (p. 2165) for two or three hours at 280° in contact with the air: $C^9H^{11}NO = C^9H^{11}N + H^2O$. It is very slightly soluble in alcohol; crystallises from benzene in somewhat irregular nacreous crystals; melts at 189°–190°. The same compound is formed by the distillation of hydroxethylene-toluidine oxalate, and as a secondary product (passing over at about 360°) in the preparation of hydroxethylene-

toluidine. In this last case the product also contains a substance melting at 155°–160°, the chemical nature of which has not yet been made out; it exhibits strong basic properties, and forms a hydrochloride which crystallises in needles.

Vinyl-toluidine, heated at 100° with *methyl iodide*, yields the compound $\left\{ \begin{smallmatrix} \text{C}^1\text{H}^1 \\ \text{C}^2\text{H}^1 \end{smallmatrix} \right\} \text{N}^2, \text{CH}^2\text{I}$, which separates from alcoholic solution in splendid dark-red crystals, yielding a nearly colourless powder. It is not attacked by caustic potash, but moist silver oxide decomposes it, with separation of silver iodide, and formation of a very strong base. From the reaction of vinyl-toluidine with methyl iodide, Demole infers that it has the constitution of a tertiary base,



Errata in Vols. VI., VII., and VIII.

The Errata here given for Vols. VI. and VII. (First and Second Supplements) apply to the first Editions of these volumes; most of them have been corrected in reprints. The asterisk in the second column denotes that the line is to be counted from the bottom.

Vol. VI.

Page	Line	Error	Correction
29	12	$C^8H^{12}N$	$(C^8H^{12}N)^2$
43	22*	61	51
85	3*	phospholybdlie	phosphomolybdie
104	24 and 34	Lippmann	Leifmann
—	24	<i>Compt. rend.</i> lxii. 426	<i>Sill. Am. J.</i> [2], xlii. 72
118	12	volatile	non-volatile
158	2	bromine	bromide
176	15	850-852	350-352
202	26*	salicin	saligenin
221	7*	arsenate	arsenite
248	9* and 12*	H^{22}	H^{22}
—	12*	H^{22}	H^{22}
264	12*	1867, pp. 342-355	1868, pp. 342-359
—	10*	1867	1868
288	31	$\frac{1}{2}H^2O$	$\frac{1}{2}H^2O$
295	7*	$C^8H^7O^4$	$C^8H^7Br^4$
—	8*	$(C^8H^7O^4)$	$(C^8H^7Br^4)$
—	15*	bromotoluene	bromoxylene
299	13*	Schrer	Storer
340	35	Penzelianite	Berzelianite
360	24*	126	227
383	23*	$CH^3O^2 + C^8H^8N$	$CH^3O^2 + 2C^8H^8N$
393	3*	P = <i>vs.</i>	P = <i>vs.</i>
398	7	Bunte	Bunte
—	8	90	96
407	2*	49	494
450	26	v.	iv.
481	24*	C^{12}	(C^{12})
571	32*	also MAGNETISM in this Suppl.	<i>dele</i>
634	12, 14	one-half	one-fourth
—	16	half	two-thirds
650	18*	products of nitric acid	products of the action of nitric acid
656	24*	action of CCl^4	action of aniline on CCl^4
670	1*	$\frac{e}{f-t}$	$\frac{e'}{f-t}$
—	16*	unit-volume between	unit-volume per degree between
675	1*	a_1	a_2
676	10	l_2	l_1
683	Table I. col. 3	17.81	117.81
—	" 29 "	1872.3	18727.3
708	" 29 "	Zn	Zn
737	8*	Werth	Weith
770	5*, 6*, 7*	$\begin{cases} H^2OH \\ HOH \\ OH \end{cases}$	$\begin{cases} CH^2OH \\ CHOH \\ COH \end{cases}$
785	8	refraction	refraction-equivalent
792	28*	27	275
861	4	v. 70	v. 396
869	3*	Ni	Co
904	22	Petalostigma	Petalostigma
977	25*	nitrite	nitrate
—	—	$C^8H^{11}NO^2$	$(C^8H^{11}NO^2)$
979	19*	$\begin{matrix} HC & CH \\ & \end{matrix}$	$\begin{matrix} HC & CH \\ & \end{matrix}$
1039	9*	411	441
1061	10	145°	54°
—	—	97°	145° (see the page)
1087	last	Oxylepidine	Oxylepidene
1097	31	$Pt^2O_3SnO^2$	$Pt^2O_3Sn^2O^2$
1103	17	-13°	-20°
—	—	0.998 at 25°	1.00 at 16°
—	—	197°	199.5°
—	24*-26*	then passes over . . . sparingly in water	is a colourless liquid; sp. gr. 0.998 at 25° ; not solidifying at -13° ; boils at 197°
1129	12	0.709	0.9709
—	16	0.9760	0.9700
1187	2	0.57	0.057

Page	Line	Error	Correction
22	6	154°	164°
27	16	15°	—15°
47	11*	allyl	allyl alcohol
129	20*	or	on
132	34	p. 14	p. 141
144	36	362	632
163	12*	$C^*HClHCl.CO^*H$	$C^*.H.H.Cl.Cl.H.CO^*H$
—	3*	721	vi. 721
176	last	V. v.	<i>dele</i>
177	1	Richter	Zincke
—	—	459	509
180	18	909	697
221	29	$C(CH^*)^*Cl$	$C(CH^*)^*Cl$
—	—	$ $	$ $
222	22	NH^*, C^*H^*	$NH(C^*H^*)^*$
225	31	$CH^*-CH^*OH-CH-CH^*OH$	$CH^*-CHOH-CH-CH^*OH$
233	11	boil	melt
234	19	$CH-C(CH^*)-CH-CH-CC^*H^*-CH$	$CH-C(CH^*)-CH-CH-C(C^*H^*)-CH$
250	14*	4·4	11·3
273	11*	Di^*Cl^*	Di^*Cl^*
312	11	as	is
325	8	odioform	iodoform
—	15*	exl. iii.	exliii.
327	16	III.	<i>dele</i>
351	14*	+ is H^*O	+ $7H^*O$
360	22*	glass	gas
384	20*	in	is
38J	14	or	on
392	6*	renders it impossible to detect	does not afford the means of detecting
394	8*	$3(FeO.SiO^*) . 4(Fe^*O^* . 3H^*O)$	$3(2FeO.SiO^*) . 2(Fe^*O^* . 3H^*O)$
—	—	$4(Fe^*)^*H^*O^*$	$2(Fe^*)^*H^*O^*$
420	27*	salts form	salt forms
427	37	sodium	iodine
423	10*	Stillbene	Stillbte, v. 435
436	2	80°	81°
—	3	omission, after (Lesimple)	boiling at 273° (Hofmeister)
484	8	butyl	propyl
489	20	xii.	xii. 406
496	12	yttria	yttria
502	2*	liii.	xxiii.
533	9	Rossin	Rossel
—	30	Bradie	Brodie
563	4 and 19	O^*	O^*
—	—	$\begin{array}{c} \text{H}-C-O \\ \\ \text{H}-C-O \end{array} \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$	$\begin{array}{c} \text{H}-C-O \\ \\ \text{H}-C-O \end{array} \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$
571	22	—	—
678	32*	342	340
707	36	79	99
749	2*	-fused	-posed
784	2*	cxlvi.	clxvi.
841	9	Ber. 943	Ber. iii. 943
886	9	773	733
893	8*	soda	potash
—	7*	Na	K
895	2	$C^*H^*NO^*$	$C^*H^*N^*O^*$
932	34	566	506
938	24	Diphenylic Phenol or Diphenol	<i>dele</i>
—	34	converts it	converts it into
—	38	132°	152°
939	29*	vil. 1034	vi. 536; Chem. Soc. J. xxvi. 1035
940	36	ammonia	ammonia and phosphoric acid
946	7*	β	α
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990	22	$Cl^*Pt \begin{array}{c} \text{PCl}^* \\ \\ \text{PCl}^* \end{array}$	$Cl^*Pt \begin{array}{c} \text{PCl}^* \\ \\ \text{PCl}^* \end{array}$
1017	34	Dichloro-	Dibromo-
1024	25*	Reimsen	Macalpine
1047	22*	567	561

ERRATA.

2173

VOL. VII.—continued.

Page	Line	Error	Correction
1065	22	Co ² K	CO ² K
1074	17*	H ¹⁹	H ¹⁹
1078	8	C ¹¹ H ¹⁸ O ⁴	C ¹¹ H ¹⁸ O ⁴
1091	7	Mactear	Mactear
1123	19 and 21	tannic	gallic
1160	1	C ¹² H ¹⁰ O ³	C ¹² H ¹⁰ O ³
1162	19	" ¹²	TI ³
—	20	potassio-platinous cyanide	thallium platinocyanide
—	21	and the corresponding barium salt	or
—	23	The potassic double salt	It
—	31	red	colourless
1178	5	C ⁷	C ⁷
—	23*	(NH ²) _m	(NH ²) _m
1186	28	[2], ix.	iv.
1196	30	C ¹² H ¹⁸ O ³	C ¹² H ¹⁸ O ³
1206	20*	R. J.	J. F.

VOL. VIII., Pt. I.

Page	Line	Error	Correction
17	7	ether	ethers
31	32	C ¹¹ H ¹³	C ¹¹ H ¹³ N
63	10	95	295
109	15	O ²	O ²
136	17	299	999
160	last	(N ¹⁰ C)	(N ¹⁰) ²
161	11	hydrocarbon	hydrocarbons
209	27*	1154	1514
261	16	C ¹¹ H ¹⁸ S ²	C ¹¹ H ¹⁸ S ²
298	24	o-	p-
317	15*	C ² H	C ² H ¹
348	24	x.	ix.
—	25, 26	O ²	O ²
364	14*	clxxxviii.	clxxxviii.
375	22*	11 ⁴	H ¹⁴
379	19	238 ^o	236 ^o
427	last	hydrochloric	hydrochloride
445	24	1758	1578
467	2*	326	213, 388
477	36	[2]	[3]
479	16	clxxvi.	clxxvi.
489	7	Homocinchonine	Homocinchonidine
495	22	omission	Beckett, Wright (<i>Chem. Soc. J.</i> xxix, 657)
521	31	Moräutsch	Moräutsch
548	11*	Opium-bases	Morphine
609	5 to 18	Perthiocyanic acid	Perthiocyanogen (see Part ii. p. 1507)
638	3	1628	1623
679	26	Diphenylene	Diphenylethylene
705	24*, 25*	CaO	CaO
720	27	N. Rep. Pharm.	N. Rep. Pharm. xxiv, 220
741	22	Schulz	Scholz
752	20*	C ¹¹ H ¹⁸ S	C ¹¹ H ¹⁸ S ²
—	27*	73 ^o	17 ^o
—	28*	-Cl ²	-CCI ²

VOL. VIII., PART II.

Page	Line	Error	Correction
875	7 and 16	Hesse	Hess
1057	30	C ² H ²	CH ²
1063	31*	Diphenylene	Diphenylethylene
1173	33	C ¹² H ¹⁸ O ³	C ¹² H ¹⁸ O ³
1235	10*	Mucilage	Plant-mucilage
1269	29	CHO	C ¹² H ¹⁰ O ²
1270	32	C ¹² H ¹⁰ N ³	C ¹² H ¹⁰ N ³
1271	25*	(C ¹² H ¹⁰)	(C ¹² H ¹⁰) ²
1282	22	at end of line insert	See further PUEKOLS (p. 1542)
1306	11	p. 1305	p. 1303
1309	23	61	616
1312	last.	crotonic	croton
1468	13	181	163

VOL. VIII., PT. II.

On p. 1807, at foot, for paragraph on Perthiocyanic Acid, read as under :—

PERTHIOCYANOGEN or **PSEUDOTHIOCYANOGEN**, $C^2H^2N^2S^2$. This, and not *perthiocyanic acid*, is the substance on which the experiments of Ponomareff (p. 602) were made. The formula of perthiocyanic acid is $C^2H^2N^2S^2$ (Atkinson). Ponomareff finds by further experiments (*Compt. rend.* lxxx. 1398) that perthiocyanic acid, heated with ammonia to a temperature not exceeding 100° (in his former experiments the heat was raised to 150° – 160°), yields a compound, $C^2H^2N^2S$, which he designates as thiamelline, together with thiomelanurenic acid, $C^2H^2N^2S^2$. Thiamelline is a white sandy powder which dissolves in 145 pts. of boiling water, and when heated with potash gives off ammonia and yields cyanate and thiocyanate of potassium. Hot strong hydrochloric acid resolves it into hydrogen sulphide, sal-ammoniac, and cyanuric acid. Nitric acid oxidises it to ammeline nitrate. Heated with ammonia, it yields a body having the properties of melamine. Thiamelline dissolves in acids and alkalis, and forms precipitates with the salts of the heavy metals. On the composition of pseudothiocyanogen see further page 1697.

END OF THE EIGHTH VOLUME.

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'The appearance of a seventh volume, being the first part of a third supplement to Mr. HENRY WATTS's valuable *Dictionary of Chemistry*, will serve to remind the studious of the marvellously rapid progress of chemical science in recent years. This first instalment of the supplement is a solid volume of upwards of 800 pages, entirely devoted, as were the previous two supplements, to recent discoveries, which are explained concisely under the old alphabetical arrangement. Thus the record of chemical discovery is brought—or rather will be brought when the second volume is published—down to the year 1877, including, however, some of the more important discoveries which have appeared in 1878. The labours of the Editor and his contributors of course lie chiefly in methodising, arranging, and reducing to the most concise form the results of experiment and investigation, English and foreign; but many of the articles embody the fruits of original research. Among the most curious as well as practically valuable articles in the present volume is that on *Flame*, contributed by Professor E. T. THORPE.'

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